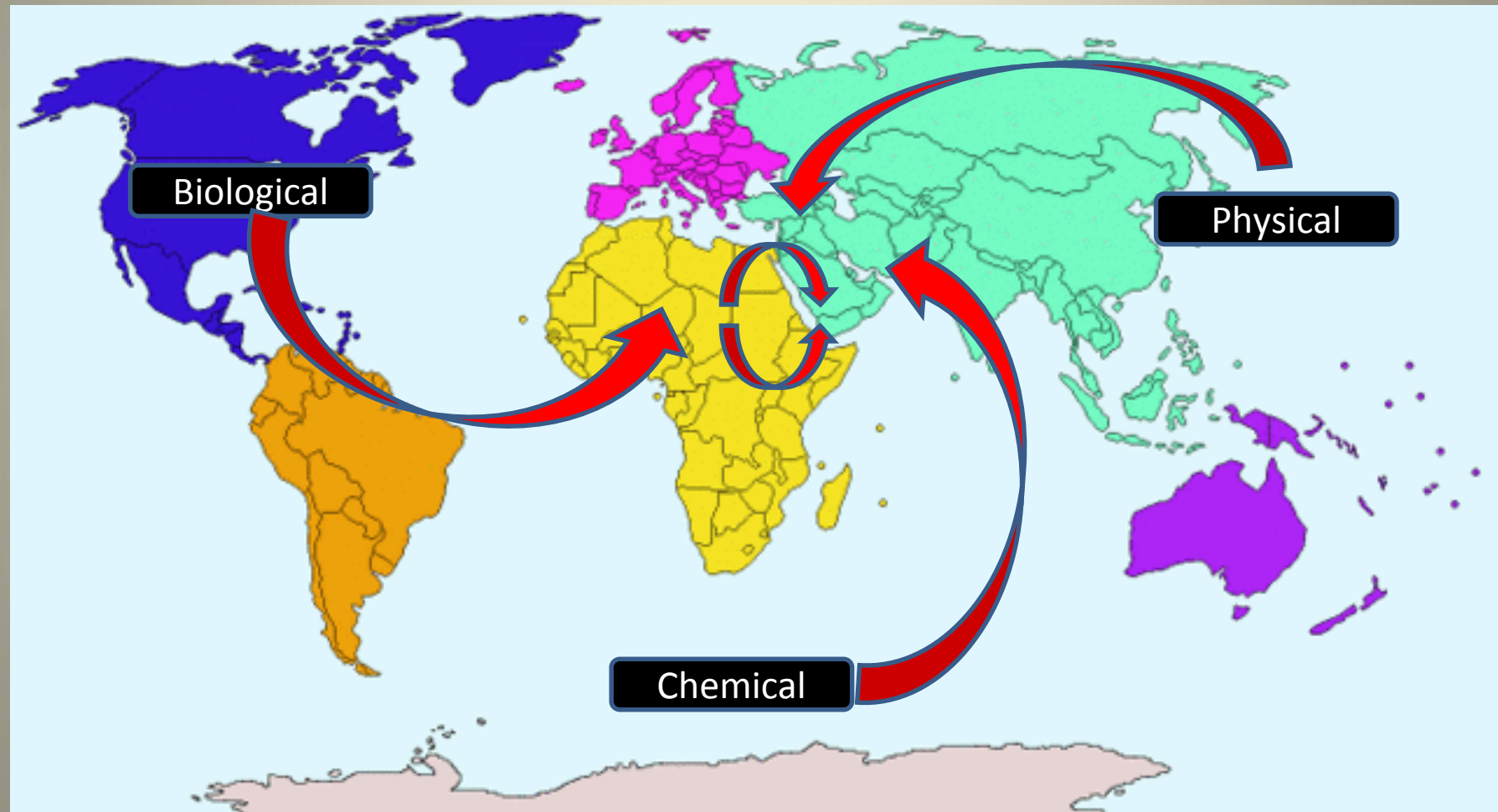


Overview of Significance of Residues and Chemical Contaminants in Milk

Michael Hickey

Dairy & Food Consultancy

Types of Residues and Contaminants found in Foods



Contaminant or Residue?

For the purposes of this presentation

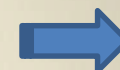
Contaminants:

Substances that are found in food, as a result of entering at any stage of the food chain. Usually they may enter food unintentionally – but occasionally due to being intentionally added with fraudulent intent.

Residues:

Substances that are found (or remain) in food as an unintended consequence of using phytosanitary products (pesticides) or veterinary drugs.

Simple Dairy Farm to Fork Chain



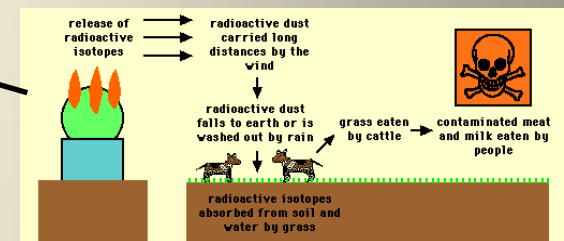
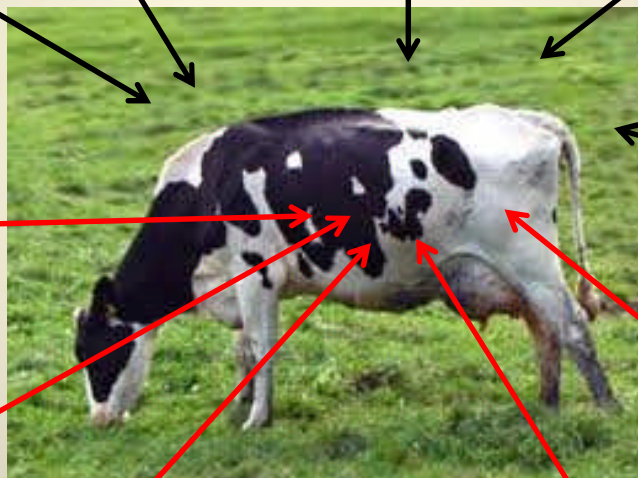
Potential Contamination Sources

- the Raw Material Source

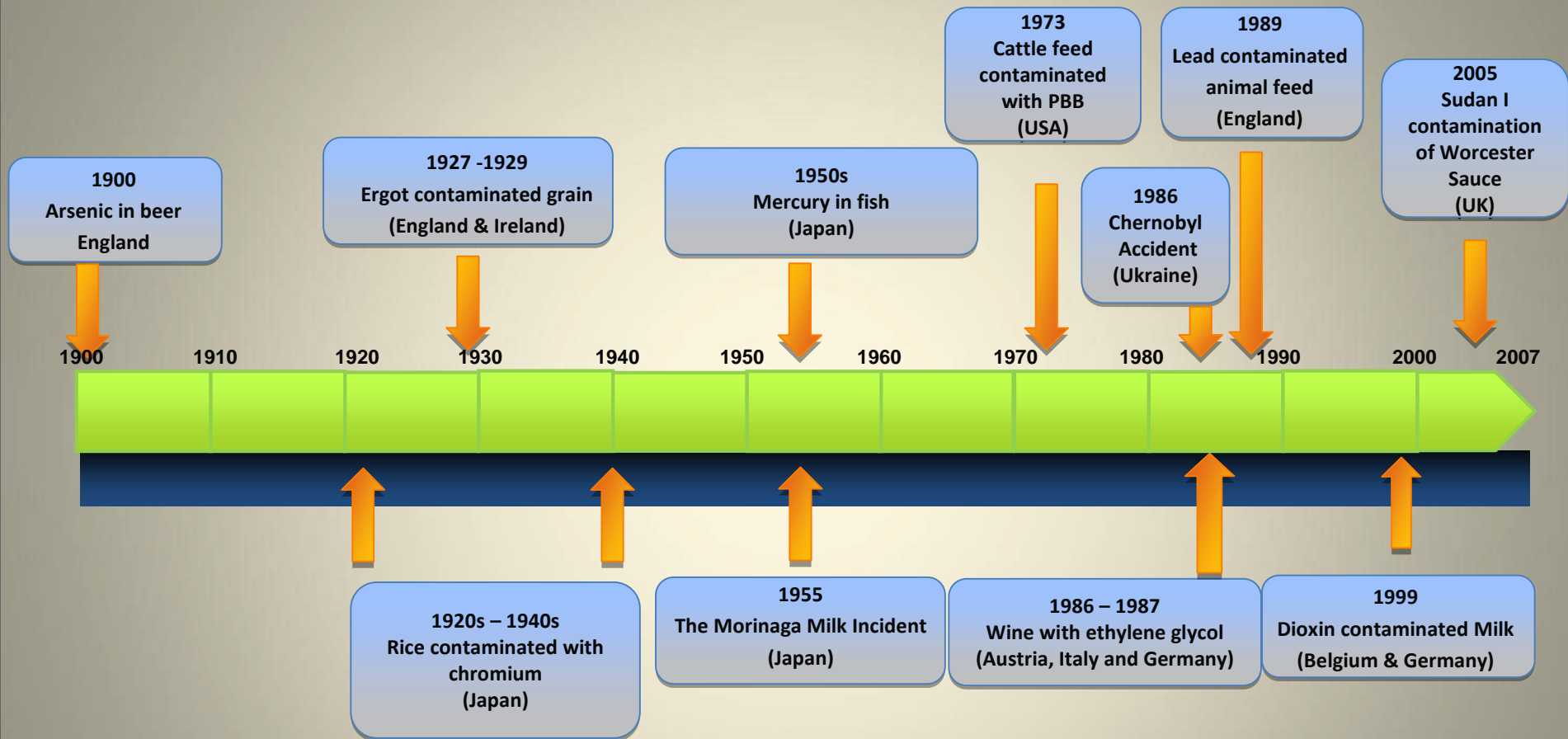


Direct →

Indirect →



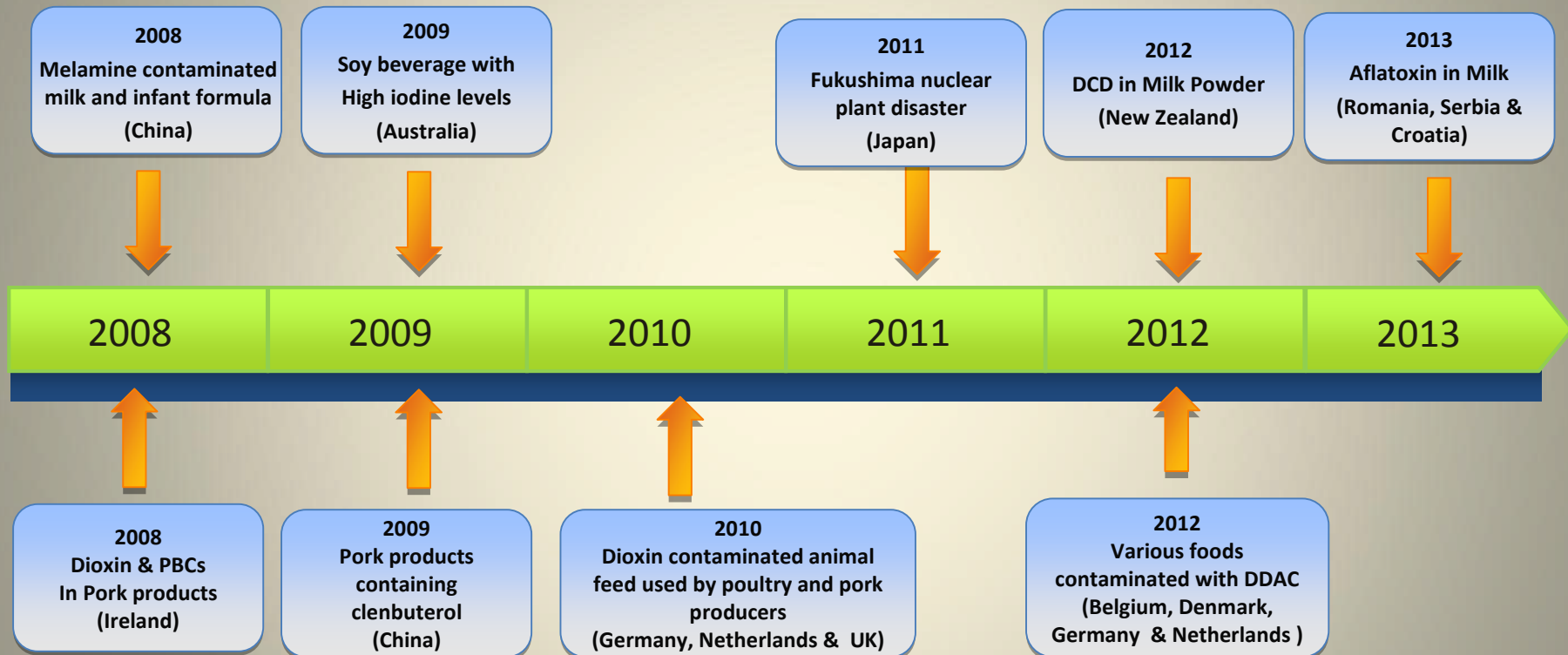
Some examples of contamination (1900 – 2007)



Morinaga Incident – recombined milk contaminated with sodium arsenate which had inadvertently contaminated a permitted food additive disodium phosphate

PBB - polybrominated biphenyl (a flame retardant)

Some examples of contamination (2008 – 2013)

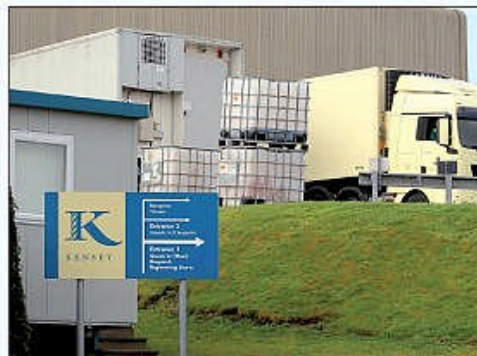
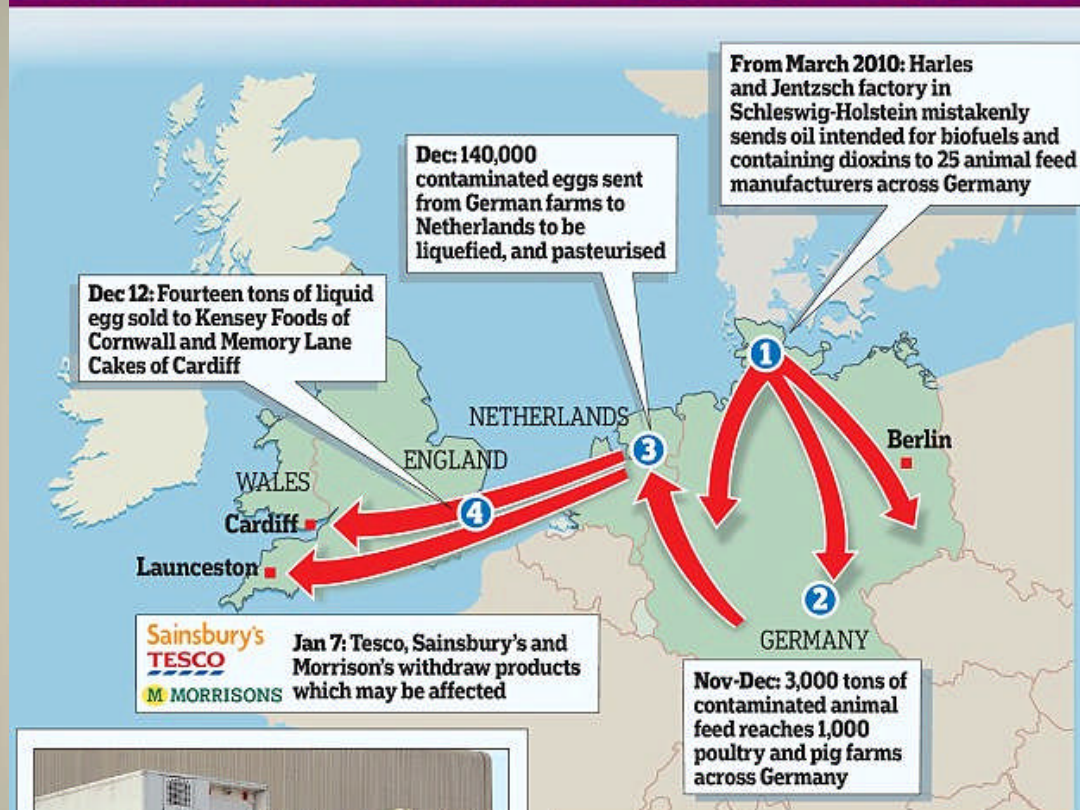


DCD – Dicyandiamide – a nitrification inhibitor that may be added to fertilizer

DDAC – Didecyldimethylammonium chloride – a Quaternary Ammonium Compound [QAC] – was authorized in EU as an active substance in plant protection products (exclusively for indoor uses for ornamental plants) – approval now withdrawn (by Implementing Reg. No 175/2013)

The EU Dioxin Case 2010

HOW THE INTERNATIONAL FOOD SCARE SPREAD

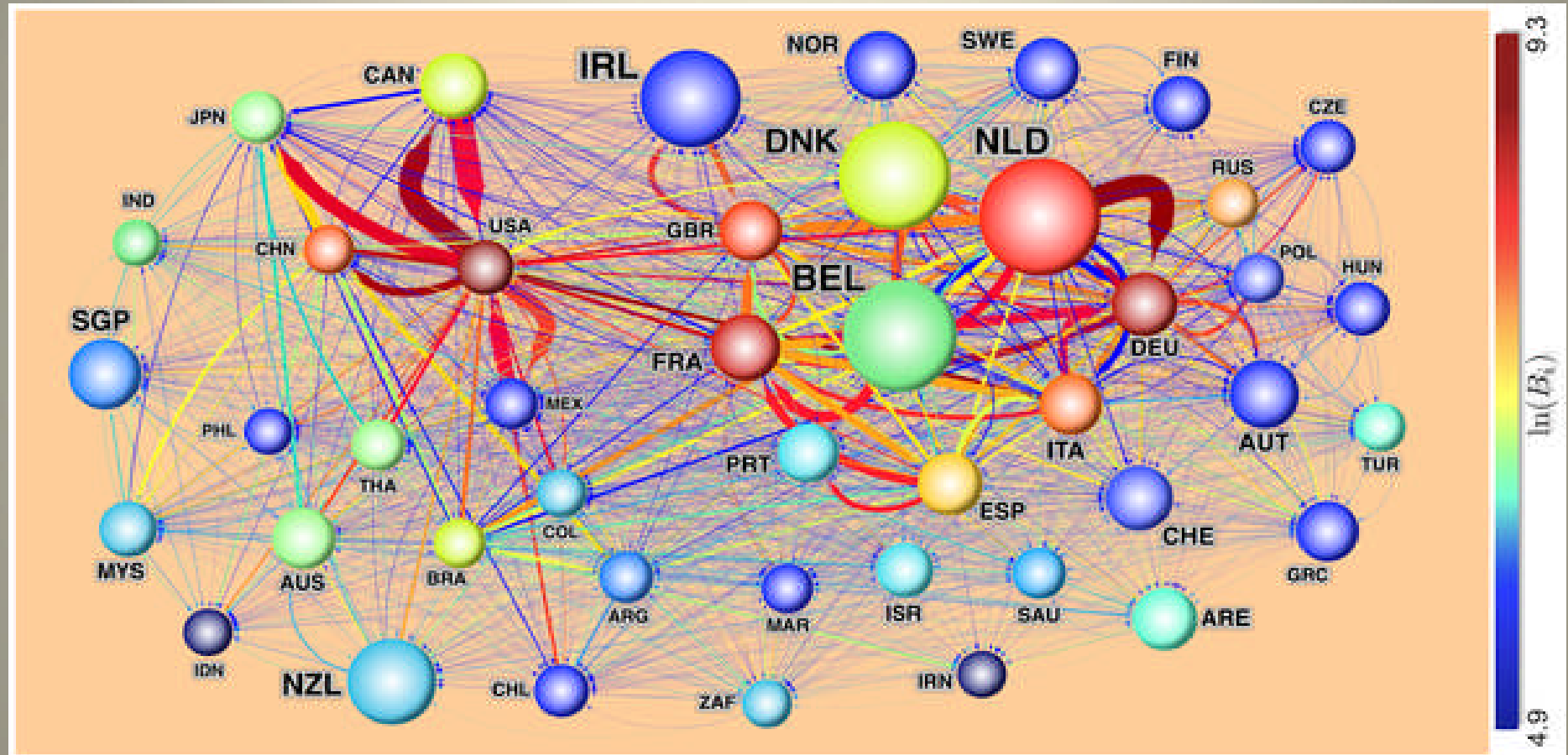


Kensey Foods, of Launceston, Cornwall, uses liquid egg to make supermarket own brand quiches.



Memory Lane Cakes, of Cardiff use eggs to make cakes for supermarkets - including Sainsbury's Chocolate Caterpillar Cake

The International Agri-Food Trade Network (IAFN Dataset 2007)

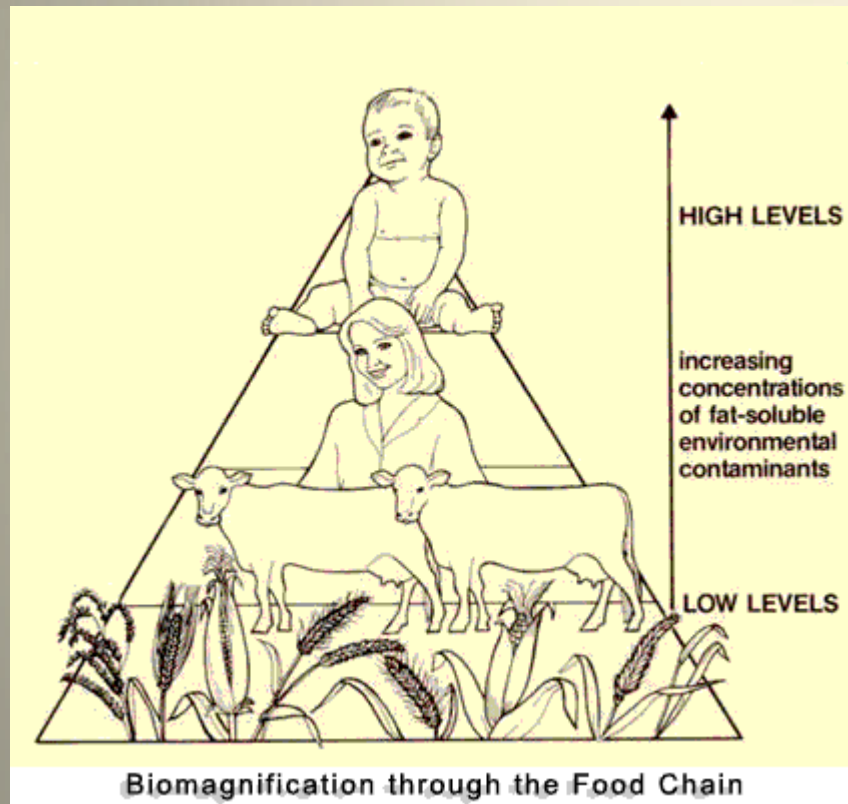


Ercsey-Ravasz M, Toroczkai Z, Lakner Z, Baranyi J (2012) Complexity of the International Agro-Food Trade Network and Its Impact on Food Safety. PLoS ONE 7(5): e37810. doi:10.1371/journal.pone.0037810
<http://www.plosone.org/article/info:doi/10.1371/journal.pone.0037810>

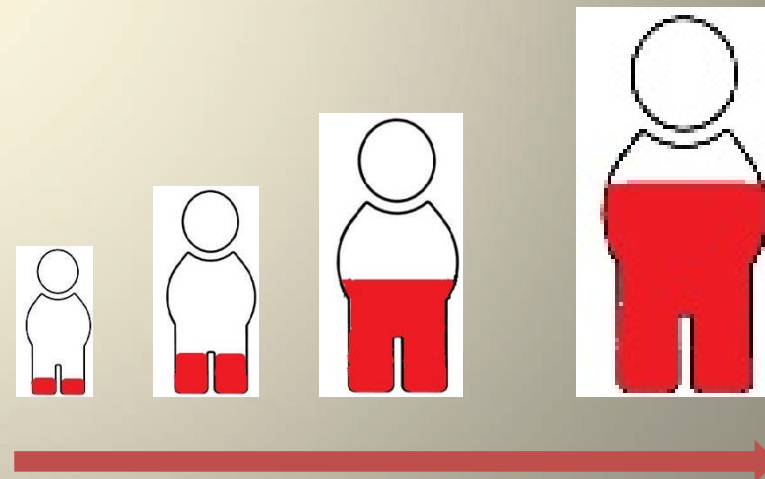
Bioconcentration

Biomagnification & Bioaccumulation

Biomagnification



Bioaccumulation



Age

POPS

The Original “Dirty Dozen” (2001)¹

Pesticides

Aldrin
Chlordane
Dichloro-diphenyl-trichloroethane (DDT)
Dieldrin
Endrin
Heptachlor
Hexachlorobenzene (HCB)
Mirex
Toxaphene

Unintended by-products

Dioxins
Furans

Industrial chemicals

Polychlorinated biphenyls (PCBs)

POPs = Persistent Organic Pollutants – all are polyhalogenated hydrocarbons

¹ Under the Stockholm Convention on Persistent Organic Pollutants - 22 May 2001

The 10 new POPs

Pesticide by-products

Chlordecone
beta-Hexachlorocyclohexane (alpha-HCH)
beta-Hexachlorocyclohexane (beta-HCH)
Lindane (gamma-HCH)
Endosulfan and related isomers

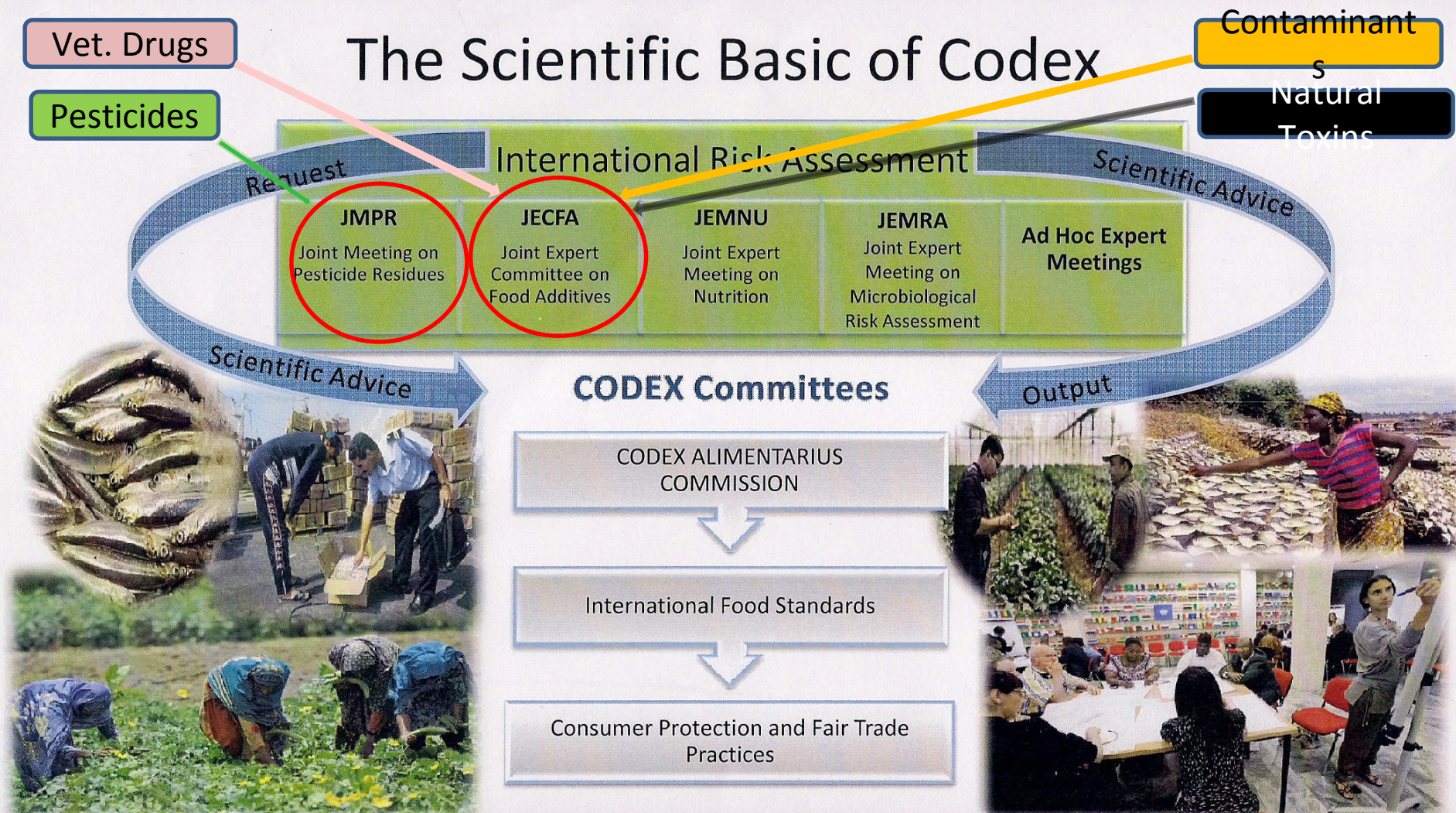
Industrial Chemicals (e.g. Flame Retardants)

Hexabromobiphenyl (HBB)
Hexabromodiphenyl ether and
heptabromodiphenyl ether
Pentachlorobenzene (PeCB) (also a Pesticide)
Perfluorooctane sulfonates and
perfluorooctane sulfonyl fluoride (PFOS)
Tetrabromodiphenyl ether and
pentabromodiphenyl ether

Elements of Risk Analysis



The Scientific Basic of Codex



Chemical Contaminants in Food - EU

Nitrates

as NO₃

Mycotoxins

Aflatoxins – B1, M1 and mixed B1/B2/G1/G2
Ochratoxin A
Patulin
Deoxynivalenol
Zearalenone
Fumonisin
T2 and H2 toxin

Metals

Lead
Cadmium
Mercury
Tin (inorganic)
[Arsenic]

Dioxins and PCBs

PAHs

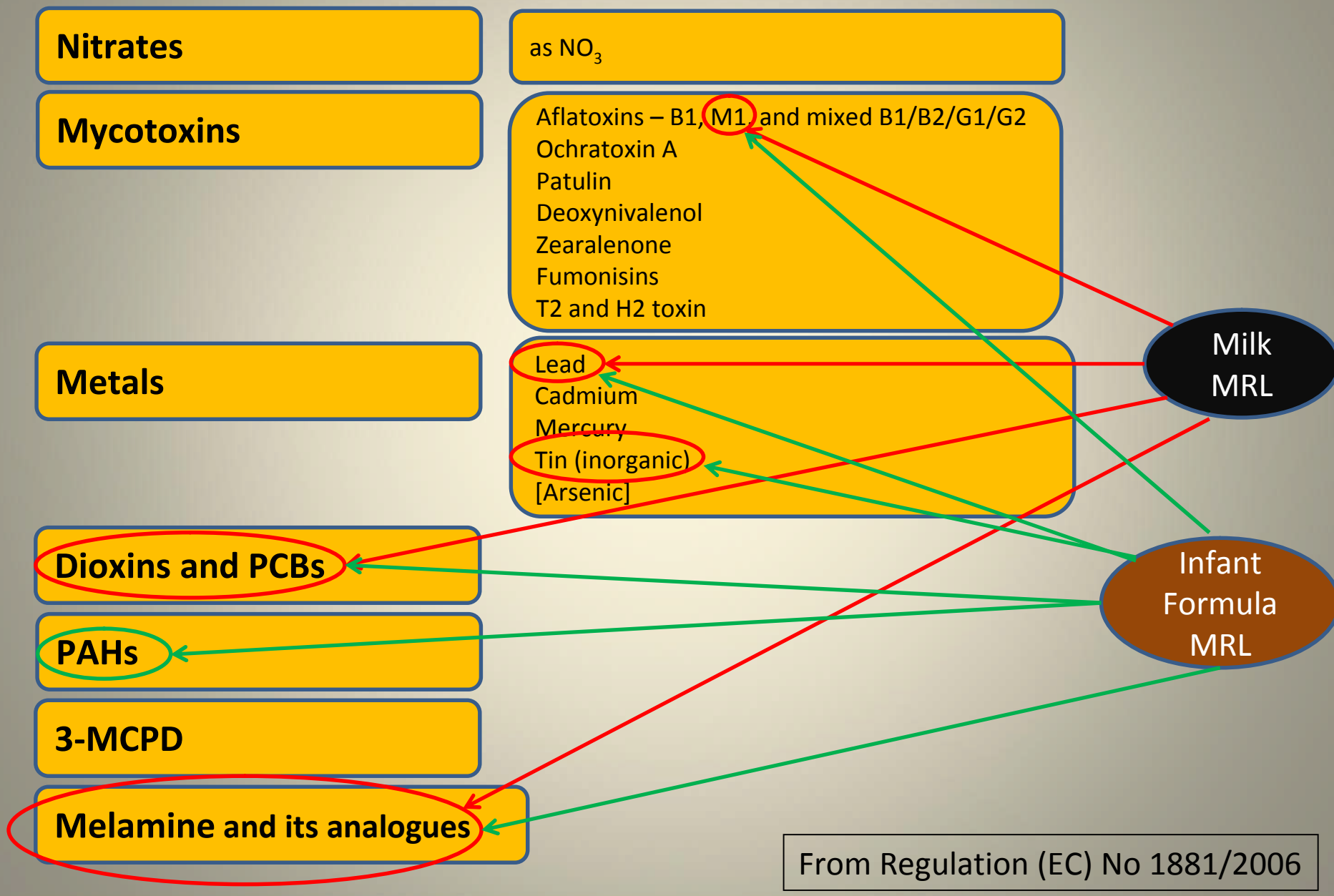
3-MCPD

Melamine and its analogues

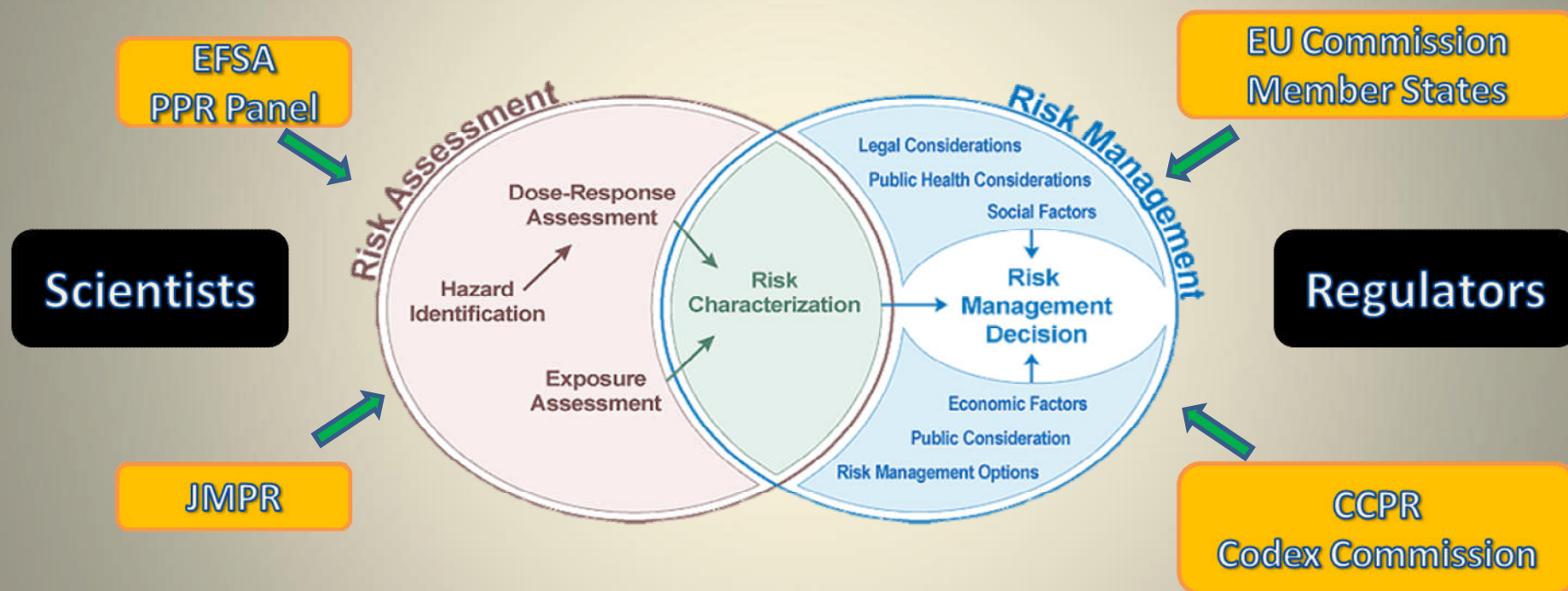
Milk
MRL

Infant
Formula
MRL

From Regulation (EC) No 1831/2003

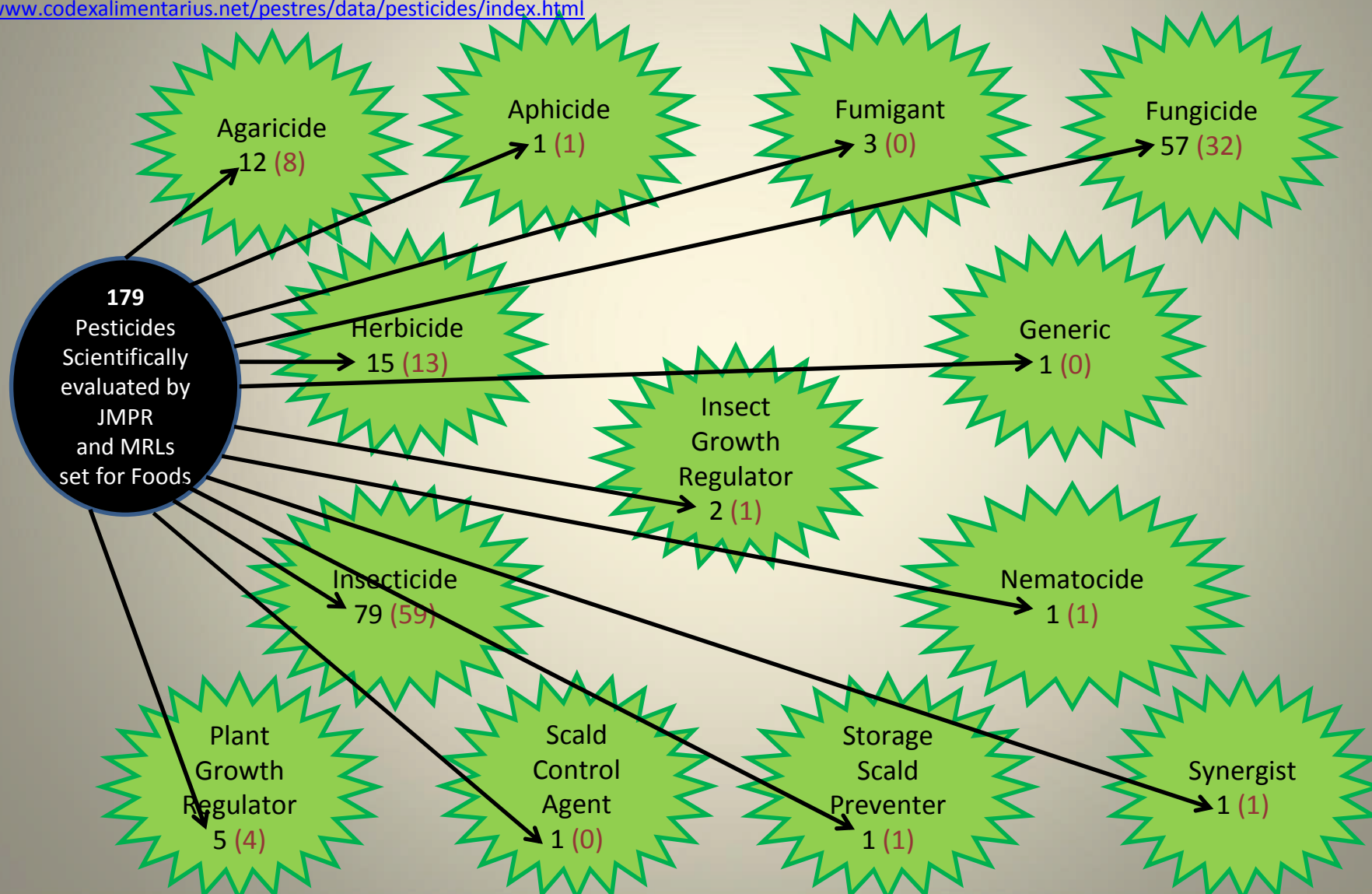


Pesticide Residue Risk Analysis



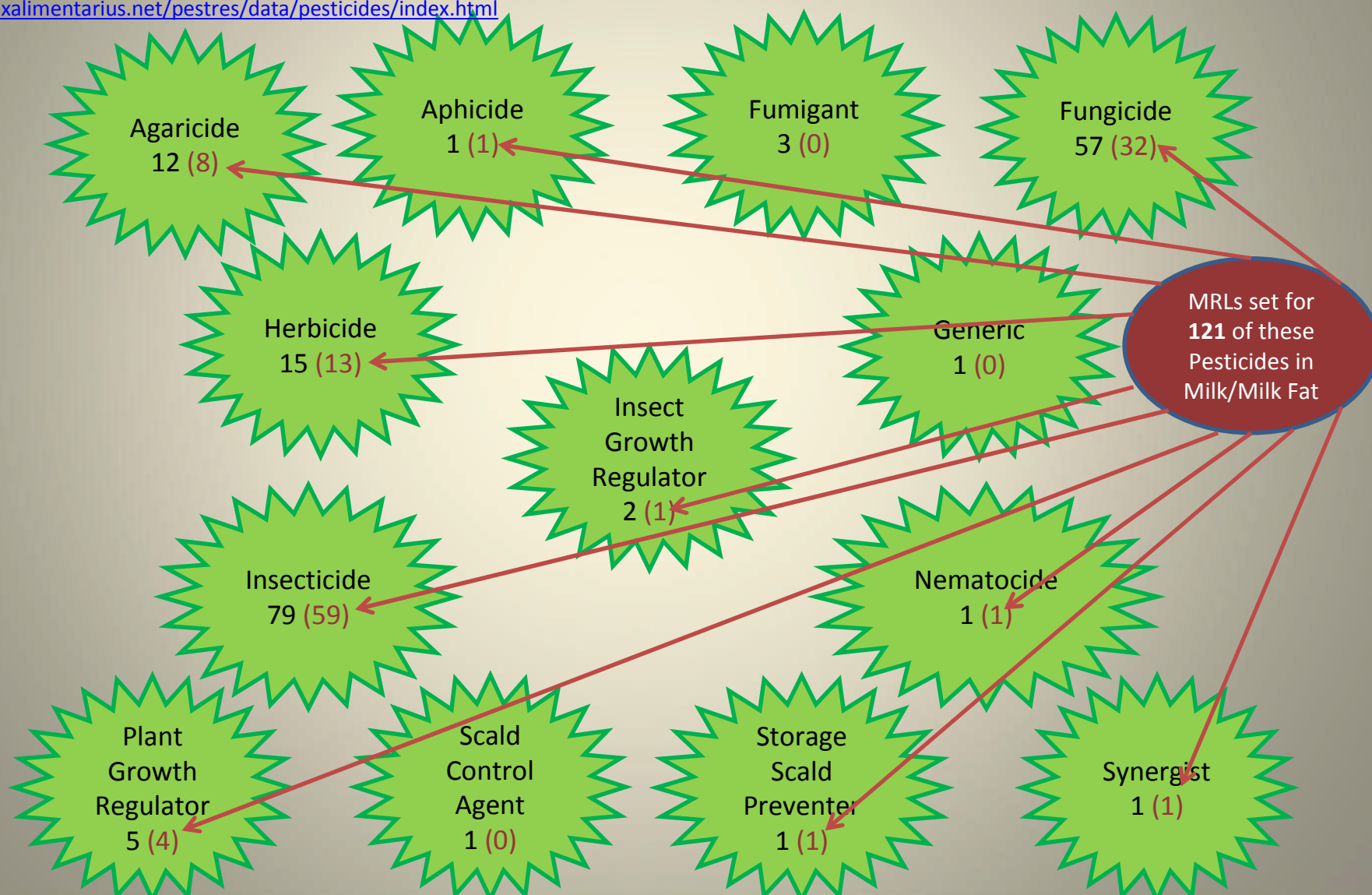
Pesticide Functional Classes (CODEX)

www.codexalimentarius.net/pestres/data/pesticides/index.html

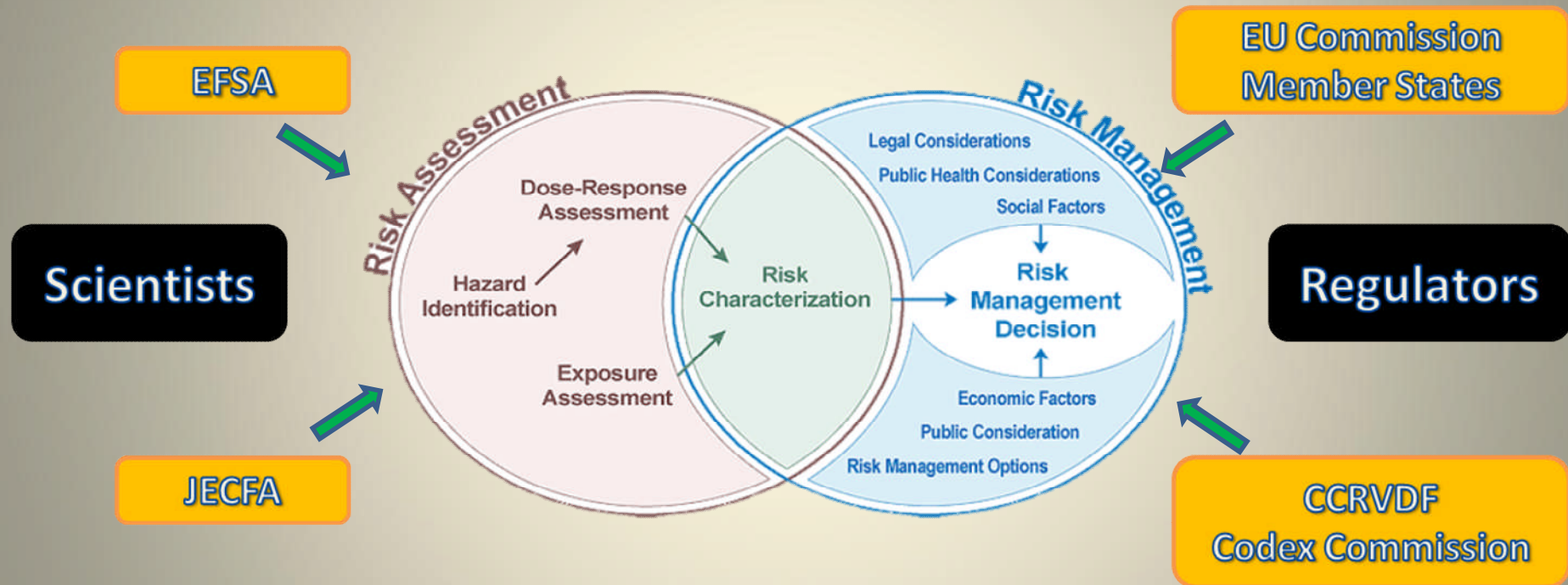


Pesticide Functional Classes (CODEX)

www.codexalimentarius.net/pestres/data/pesticides/index.html



Veterinary Drug Residue Risk Analysis



Functional Categories of Veterinary Drugs (CODEX)

Adrenoceptor
Agonist
1 (1)

Anthelmintic
11 (6)

Antimicrobial
22 (15)

**59 MRLs in Total
set for Foods**

Antiprotozoal3
(1)

β -Adrenoceptor
blocker
1 (0)

**31 MRLs for set for
Milk**

Growth
promoter
2 (0)

Glucocorticosteroid
1 (1)

Insecticide
8 (5)

Production aid
7 (0)

Trypanocide
2 (2)

Tranquilizer
1 (0)

Codex Alimentarius Commission
Maximum Residue Limits for Veterinary Drugs in Foods
Updated as at the 35th Session of the Codex Alimentarius Commission (July 2012)

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Veterinary Drug	Page	Veterinary Drug	Page
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Febantel/Fenbendazole/Oxfendazole	19	Triclabendazole	39
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Flumequine	21		

**Residues of ~ 90
Veterinary Drugs
evaluated by JECFA**

**59 MRLs in Total
set for Foods**

**31 MRLs for set for
Milk**

rBST not included (yet!)

EU Pesticides Database

Includes Approved, Non-approved, Pending and substances that are not plant protection products

Active substances

Select your criteria

Category

Status

Class. (Dir. 67/548/EEC)

Class. (Reg. 1272/2008)

Authorisations

Legislation

from to/until

ADI

ARfD

AOEL

Approval date

Expiration date

(4Z-9Z)-7,9-Dodecadien-1-ol
(E)-10-Dodecen-1-yl acetate
(E)-11-Tetradecen-1-yl acetate
(E)-2-Methyl-6-methylene-2,7-octadien-1-ol (myrcenol)
(E)-2-Methyl-6-methylene-3,7-octadien-2-ol (isomyrcenol)
(E)-5-Decen-1-ol
(E)-5-Decen-1-yl acetate
(E)-8-Dodecen-1-yl acetate
(E)-9-Dodecen-1-yl acetate
(E,E)-7,9-Dodecadien-1-yl acetate
(E,E)-8,10-Dodecadien-1-ol
(E,E)-8,10-Dodecadien-1-yl acetate
(E,Z)-2,13-Octadecadien-1-yl acetate
(E,Z)-4,7-Tridecadien-1-yl acetate
(E,Z)-7,9-Dodecadien-1-yl acetate
(E,Z)-8,10-Tetradecadien-1-yl
(E,Z)-8-Dodecen-1-yl acetate
(E,Z)-9-dodecen-1-yl acetate; (E,Z)-9-Dodecen-1-ol; (Z)-11-Tetradecen-1-yl acetate
(IR)-1,3,3-Trimethyl-4,6-dioxatricyclo[3.3.1.0^{2,7}]nonane (lineatin)
(Z)-11-Hexadecen-1-ol
(Z)-11-Hexadecen-1-yl acetate
(Z)-11-Hexadecenal
(Z)-11-Tetradecen-1-yl acetate
(Z)-13-Hexadecen-11-yn-1-yl acetate
(Z)-13-Octadecenal
(Z)-3-Methyl-6-isopropenyl-3,4-decadien-1-yl acetate
(Z)-3-Methyl-6-isopropenyl-9-decen-1-yl acetate

1297 entries found

Total of 1297 Substances

http://ec.europa.eu/sanco_pesticides/public/?event=activesubstance.selection

EU Pesticides Database

Active substances

Select your criteria

Category All

Status Approved

Class. (Dir. 67/548/EEC) -

Class. (Reg. 1272/2008) -

Authorisations -

Legislation -

ADI All from All to/until

ARfD All

AOEL All

Approval date All

Expiration date All

Search Reset

Find substance

Show details

Export list

alphabetically

(E)-11-Tetradecen-1-yl acetate
(E)-5-Decen-1-ol
(E)-5-Decen-1-yl acetate
(E)-8-Dodecen-1-yl acetate
(E,E)-7,9-Dodecadien-1-yl acetate
(E,E)-8,10-Dodecadien-1-ol
(E,Z)-2,13-Octadecadien-1-yl acetate
(E,Z)-7,9-Dodecadien-1-yl acetate
(E,Z)-8-Dodecen-1-yl acetate
(Z)-11-Hexadecen-1-ol
(Z)-11-Hexadecen-1-yl acetate
(Z)-11-Hexadecenal
(Z)-11-Tetradecen-1-yl acetate
(Z)-13-Hexadecen-11-yn-1-yl acetate
(Z)-13-Octadecenal
(Z)-7-Tetradecenal
(Z)-8-Dodecen-1-ol
(Z)-8-Dodecen-1-yl acetate
(Z)-9-Dodecen-1-yl acetate
(Z)-9-Hexadecenal
(Z)-9-Tetradecen-1-yl acetate
(Z,E)-7,11-Hexadecadien-1-yl acetate
(Z,E)-9,12-Tetradecadien-1-yl acetate
(Z,Z)-7,11-Hexadecadien-1-yl acetate
(Z,Z,Z)-7,13,16,19-Docosatetraen-1-yl isobutyrate
1-Decanol
Methyl-cyclopropene

440 entries found

Total of just 440 APPROVED Substances

EU Pesticides Database

Active substances

Select your criteria

Category: HB - Herbicide

Status: Approved

Class. (Dir. 67/548/EEC): -

Class. (Reg. 1272/2008): -

Authorisations: -

Legislation: -

ADI: All

ARfD: All

AOEL: All

Approval date: All

Expiration date: All

Search Reset

Find substance

Show details

Export list

alphabetically

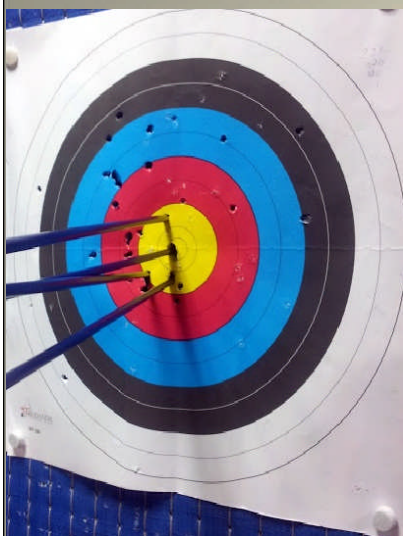
128 entries found

2,4-D
2,4-DB
Acetic acid
Aclonifen
Amidosulfuron
Amitrole (aminotriazole)
Azimsulfuron
Beflubutamid
Benfluralin
Bensulfuron
Bentazone
Bifenox
Bispyribac
Bromoxynil
Capric acid (CAS 334-48-5)
Caprylic acid (CAS 124-07-2)
Carbetamide
Carfentrazone-ethyl
Chloridazon (aka pyrazone)
Chlorotoluron
Chlorpropham
Chlorsulfuron
Clethodim
Clodinafop
Clomazone
Clopyralid
Cycloxydim

128 APPROVED Herbicide Substances

Targeted Sampling Approach

The National Residue Plan



Aimed at:-

Detecting of the illegal use of prohibited substances.

Monitoring compliance with the specified MRLs for veterinary drugs, pesticides, mycotoxins, heavy metals etc.

Monitoring levels of environmental contaminants.

Sampling focus:-

Most samples (c. 80%) are taken in accordance with criteria designed to target animals or products, which are more likely to contain illegal residues

However sampling may also be conducted in specific cases where the presence of illegal residues was suspected

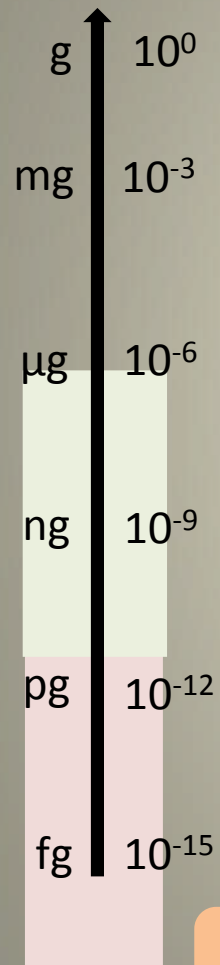
National Residue Plan (Ireland) for Milk

GROUP A – Substances having anabolic effect and unauthorised substances		Milk
A1	Stilbenes and derivatives	
A2	Antithyroid agents	
A3	Steroids (natural and synthetic)	
A4	Resorcylic acid lactones (incl. zeranol)	
A5	Beta-agonists	
A6	Compounds in Annex IV of Reg. 2377/90 (e.g. chloramphenicol, nitrofurans etc.)	✓
GROUP B – Veterinary Drugs and Contaminants		
B1	Antibacterial substances, incl. sulphonamides, quinolones, tetracyclines.	✓
B2a	Anthelmintics (parasitic worms/helminths)	✓
B2b	Anticoccidals	
B2c	Carbamates and pyrethroids	
B2d	Sedatives	
B2e	Non-steroidal anti-inflammatory drugs (NSAIDs)	✓
B2f	Other pharmacologically active substances (e.g. teflubenzuron, diflubenzuron)	
B3a	Organochloride compounds (incl. PCBs)	✓
B3b	Organophosphorus compounds	✓
B3c	Chemical elements (lead, cadmium, mercury, arsenic)	✓
B3d	Mycotoxins	✓
B3e	Dyes (e.g. malachite green)	
B3f	Others (brominated flame retardants, PAHs)	

Ref: National Food Residue Database Report 2010/11. M. Danagher & J. Rae,J.

see http://nfrd.teagasc.ie/pdf/NFRD_Annual_Report_2011.pdf

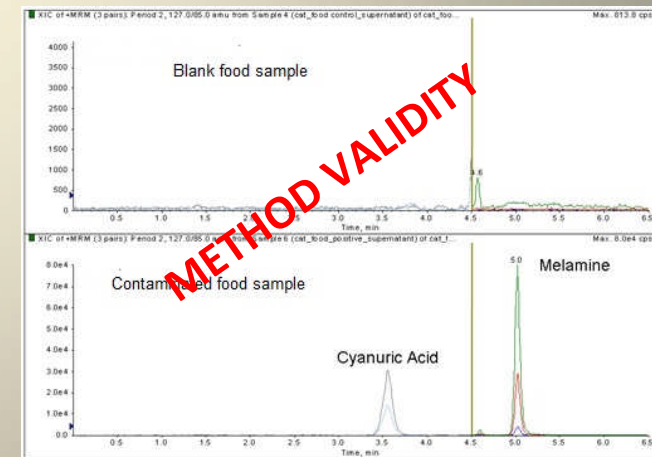
Analysis Challenges



The Level of Contamination



Food matrix complexity



Verification and validation

Biomarker Methodology

Requires demonstration of a quantitative relationship between intake of a substance and the amount of the substance or a metabolite in the body tissue or fluid of an animal - e.g., in blood, adipose tissue, urine, or milk

BioCop Project (2005 – 2009)¹
detecting chemical contaminants in food

- Involved measuring of the effect of the contaminant(s) rather than the more traditional single target compound concentrations
- Developed using rapid and efficient transcriptomics, proteomics and biosensor-based technologies
- Examples include detection of:-
 - Pesticides
 - Mycotoxins such as produced by fungi
 - Therapeutic drugs (growth promoters, quinolone antimicrobials)
 - Endocrine disrupters (phytoestrogens)

¹ For more see http://www.teagasc.ie/publications/2009/1075/biocop_detecting_chemical_contaminants_in_food_5442.pdf
or <ftp://ftp.cordis.europa.eu/pub/food/docs/elliott.pdf>

Acknowledgement

Some concepts and illustrations used herein are based on a presentation entitled
FOOD SAFETY MANAGEMENT SYSTEM FOR CONTAMINANTS
AND DRUG RESIDUES IN THE DAIRY PRODUCTS
by Prof. Dr. Bruno LE BIZEC, École Nationale Vétérinaire,
Agroalimentaire et de l'Alimentation Nantes-Atlantique
given at the **2013 IDF World Dairy Summit** in Yokohama,
Japan.

However, the views and opinions expressed herein are my own and should not be taken as being those of Dr. LE BIZEC and his co-workers.

THANK YOU