

# Strategies and measures to reduce the risks of trading not compliant fruit & vegetable products

## Requirements on a globally operating residue lab.

**Thies Claussen**

**Eurofins Food GmbH | Dr. Specht Laboratorien**

**Hamburg - Germany**

- The European market for fruit & vegetable
- The demand of the consumer (“High Tech - High Touch”)
- The requirements of the market
- Recently occurred food safety incidences their economical and reputational impact
- Brief excurses to Quarternary Ammonium Compounds  
Morpholine, CCC, DDAC/BAC, Perchlorate, etc.
- Conclusion for all stakeholders along the fruit & veg supply chain

# European Fruit & Veg market



Physical Map of the World, April 2007

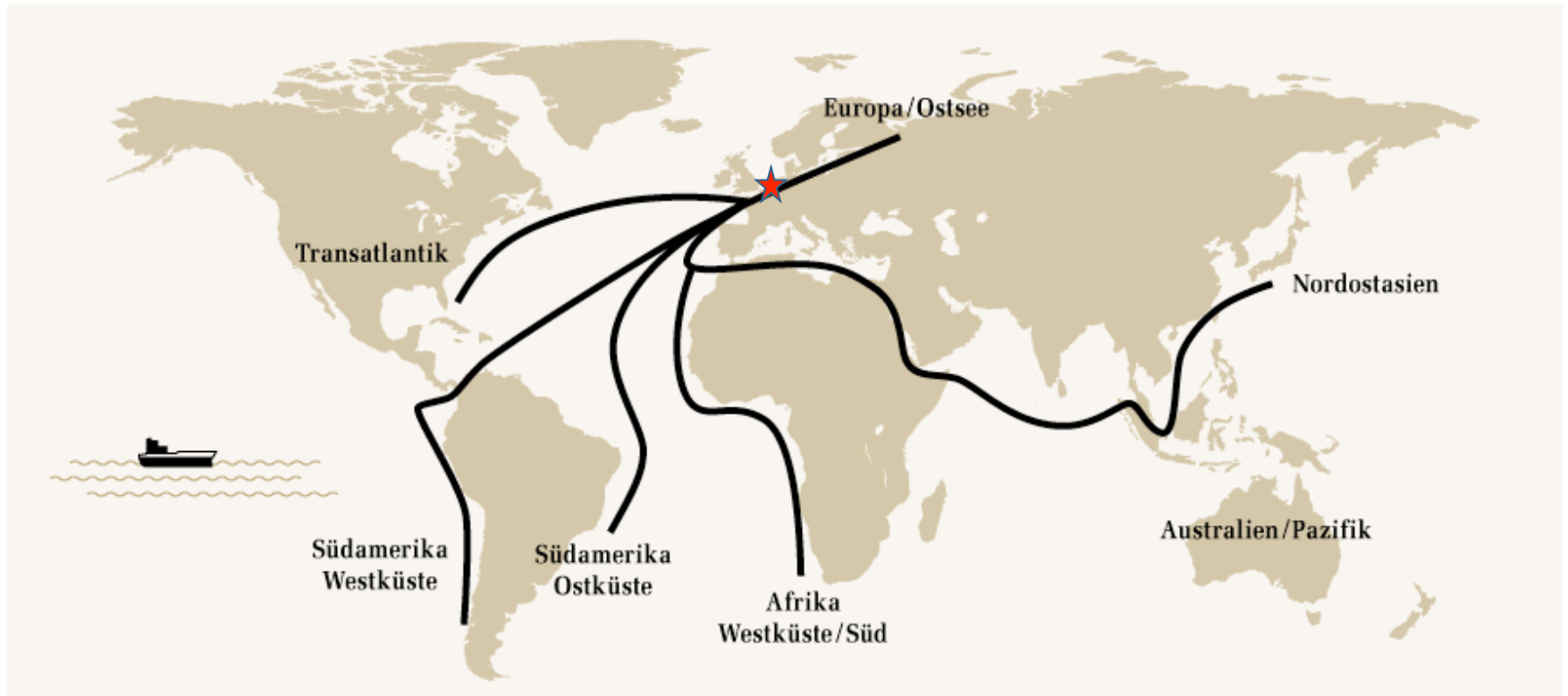
AUSTRALIA Independent state  
Bermuda Dependency or area of special sovereignty  
Sicily / ANNEX Island / island group  
★ Capital  
Scale 1:15,000,000  
Robinson Projection  
standard parallels 30° N and 30° S



April 2007  
© 2007 by Thomson Digital  
All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, without the prior written permission of Thomson Digital.

- over 700 million people in Europe
- Fruit & Vegetable market in the EU is worth 50 billion €
- The F&V supply chain has an estimated turnover >120 billion €
- The EU is the world's second largest producer, the EU is also the second largest importer of F&V
- Germany alone consumes over 5,5 billion tons fruit&veg

(Source: European Parliament report 08/2013 and GfK data)



➤ ➔ Benelux ports are the main entry into central Europe

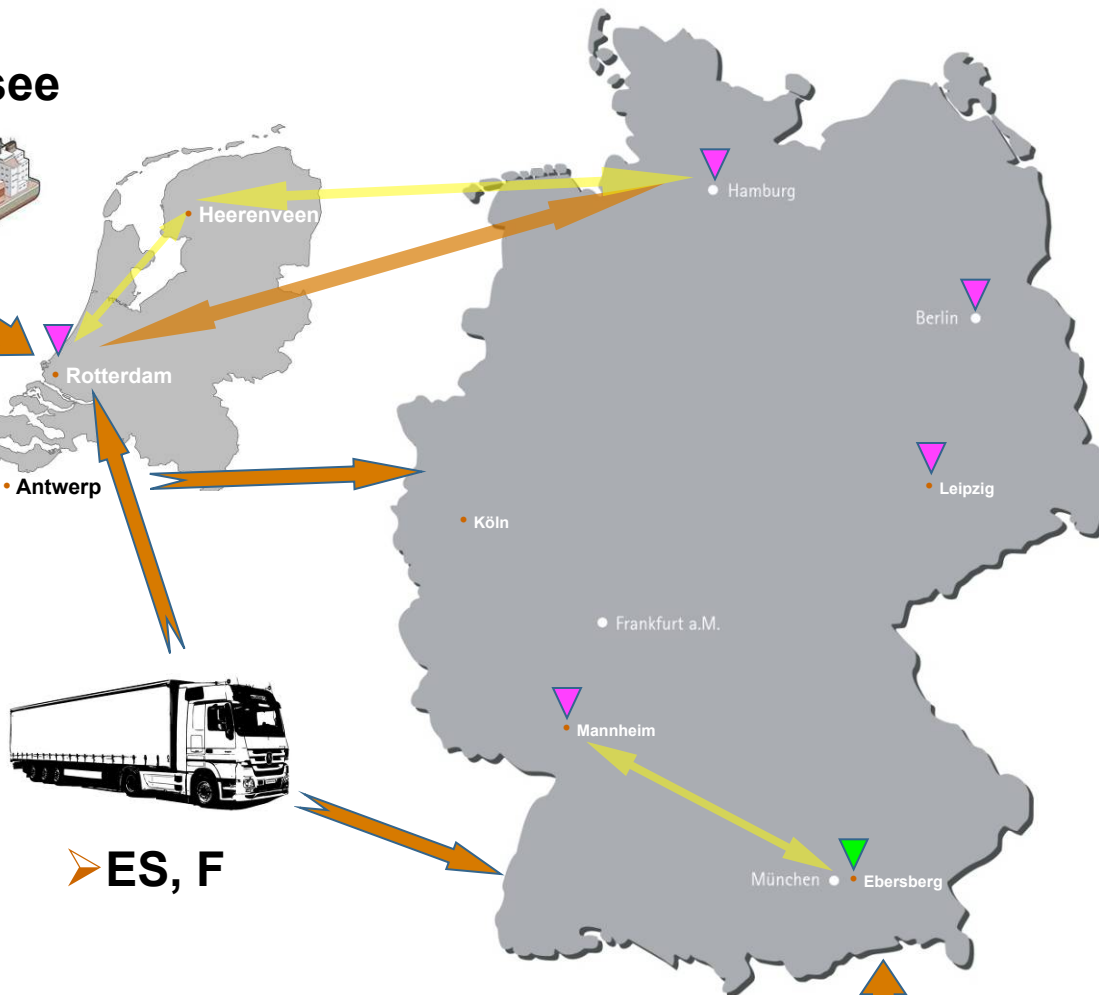
# Supply chain Fruit&Veg



## ➤ Overseas



© www.123f.com



➤ ES, F

↔ ➤ Logistic

↔ ➤ Datatransfer

▼ ➤ Laboratories

▼ ➤ DC's

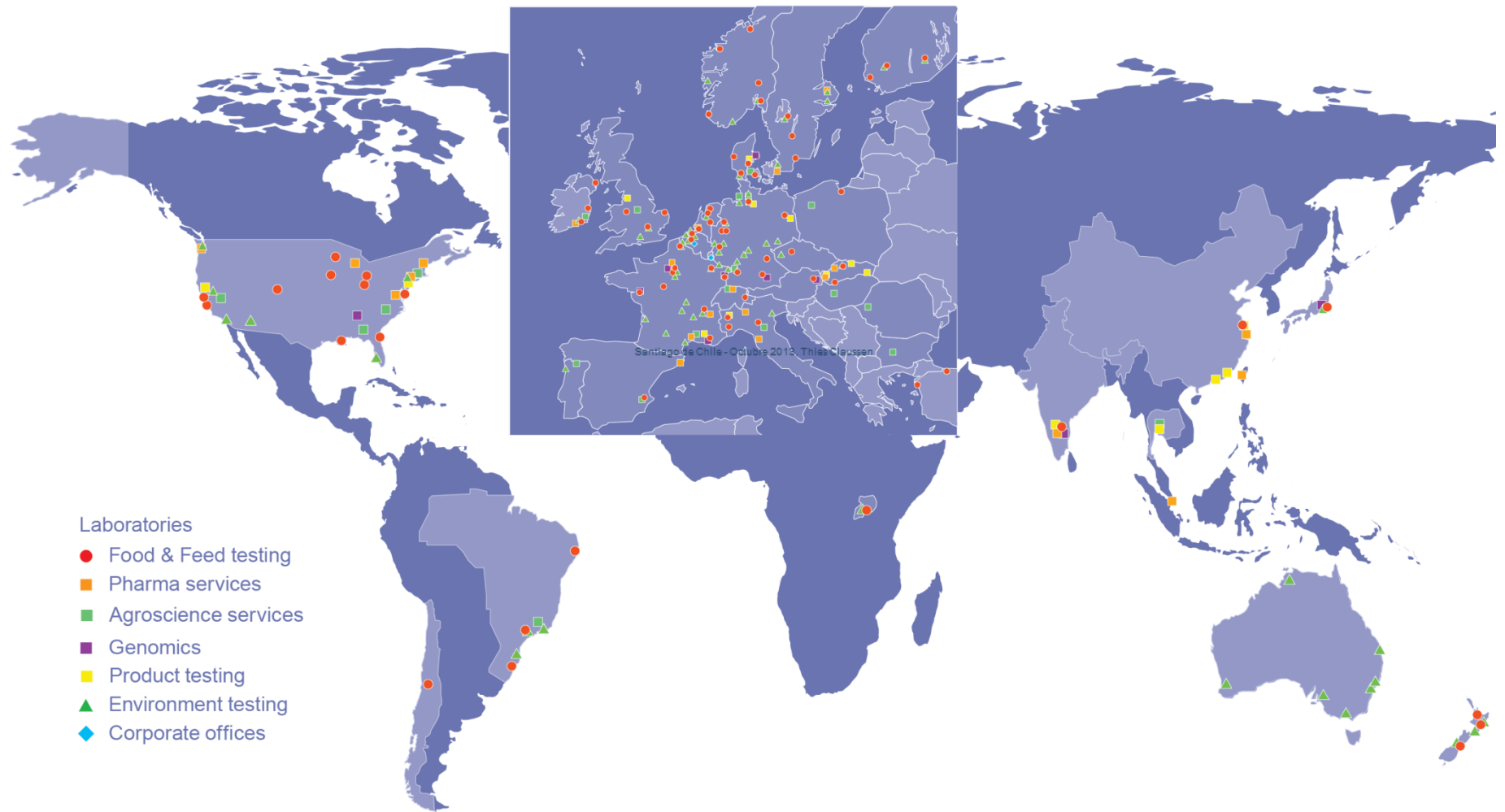
➔ ➤ Import Routes



hies Claussen

➤ IT,  
GR

# Eurofins has a global Net of specialised laboratories



## What drives the retail ?



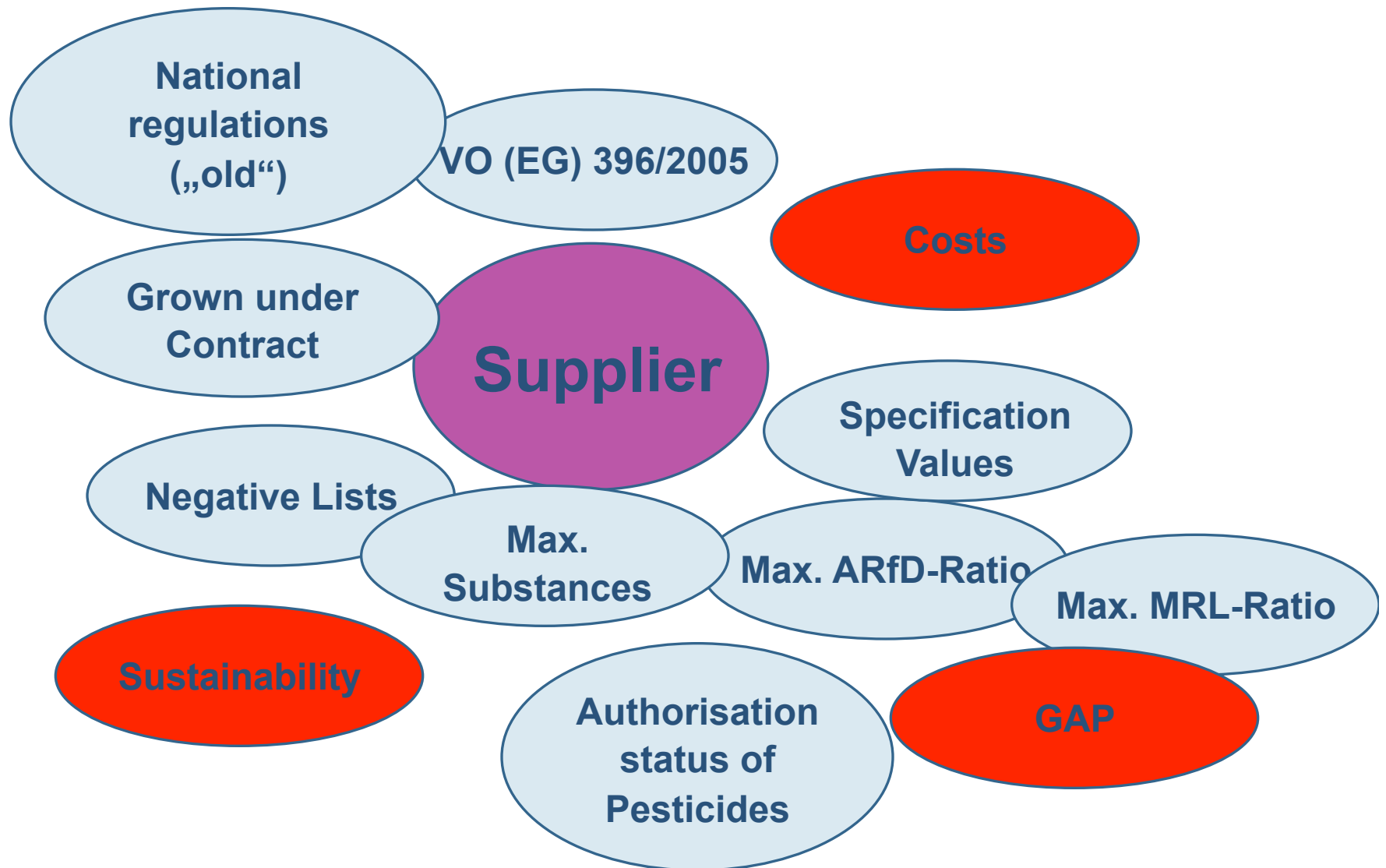
**Campaigns of NGO's  
and Media (high tech /  
high touch)**

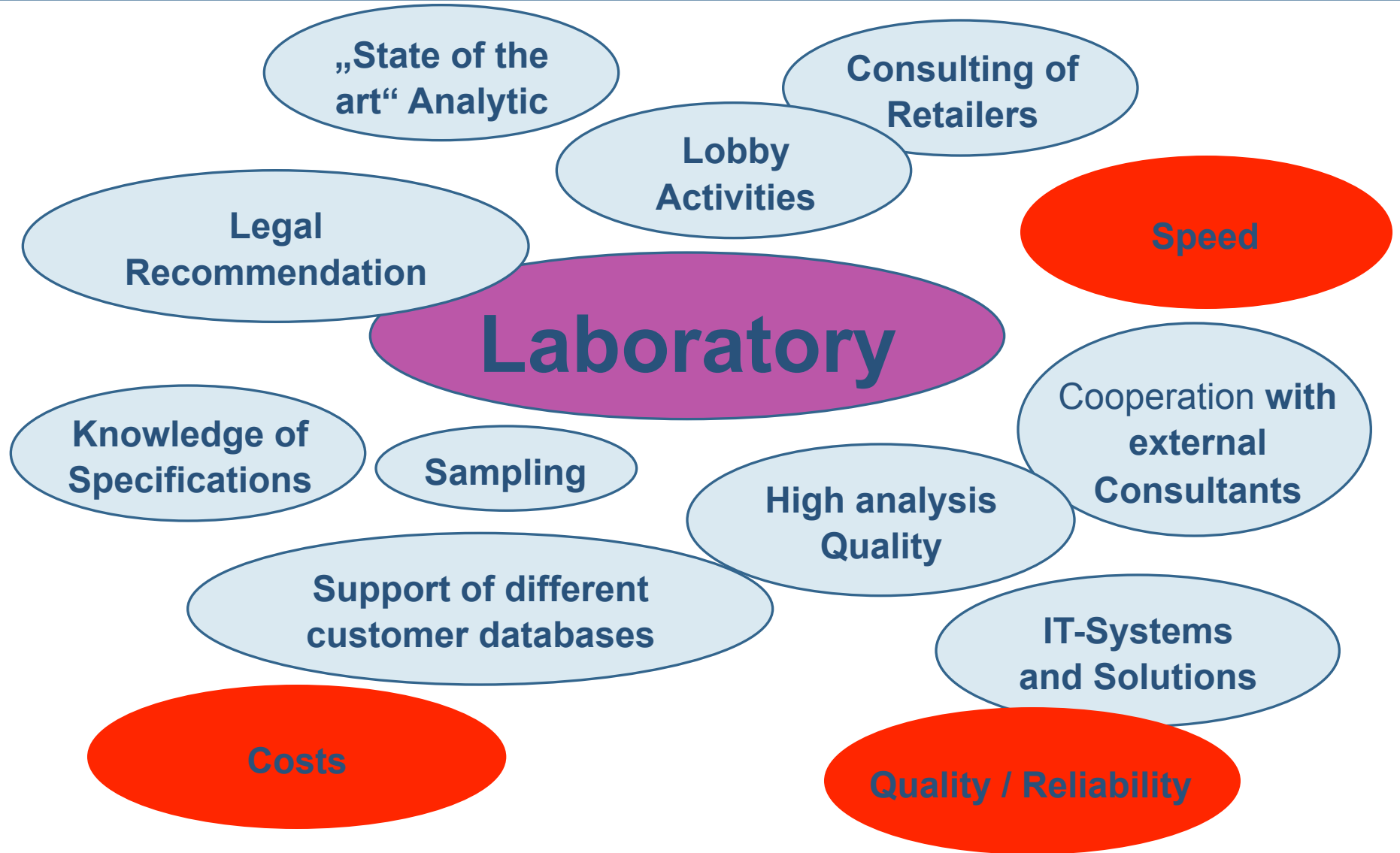


# Overview: Retail Specifications Fruits and Vegetables



Max. MRL-Ratio	70 %	70 % <i>private Brand:</i> 50%	70 % <i>private Brand:</i> 50 %	33,3 % (EC) 396/2005 and RhmV)	33,3 %
Specification Values: Matrix/ Country	-	-	-	Yes	-
Max. MRL- $\Sigma$ -Ratio	80 %	-	-	-	-
Max. ARfD-Ratio	100 %	70 %	100 %	100 %	100 %
Max. ARfD- $\Sigma$ -Ratio	80 %	-	-	-	100 %
amount* or kind** of a. i.	Yes (*)	Yes (**)	Yes (**)	-	-





## Laboratory in 1980



# Laboratory 2013



## 1400 active Pesticide substances known worldwide European Review Process



In 1993 the European Commission launched the work program on the Community-wide review for all active substances used in plant protection products within the European Union. In this review process, each substance had to be evaluated as to whether it could be used safely with respect to human health (consumers, farmers, local residents and passers-by) and the environment, in particular groundwater and non-target organisms, such as birds, mammals, earthworms, bees.

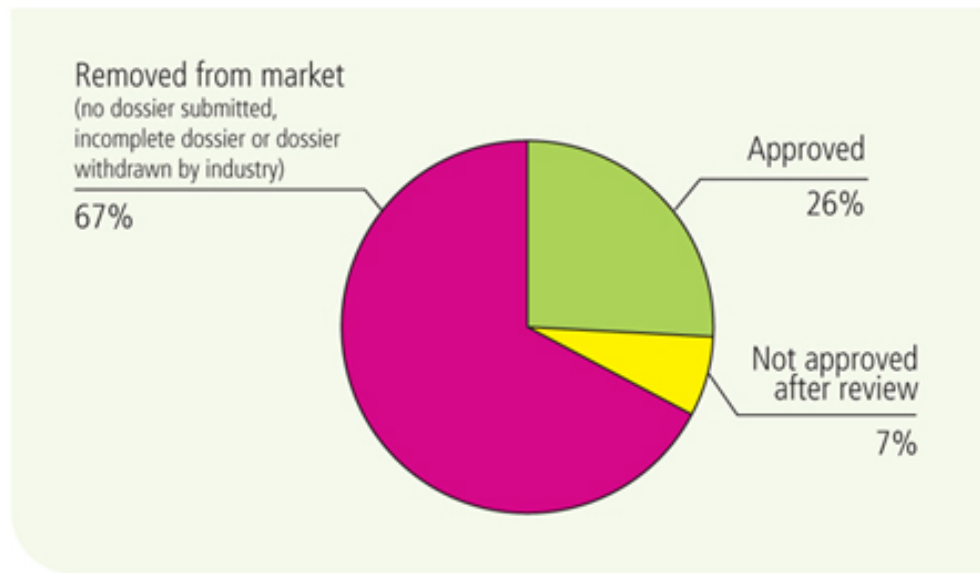
**Placing of plant protection products on the EU market was regulated by Council Directive 91/414/EEC.**

**This Directive was replaced with effect from 14 June 2011 by Regulation (EC) No 1107/2009 .**

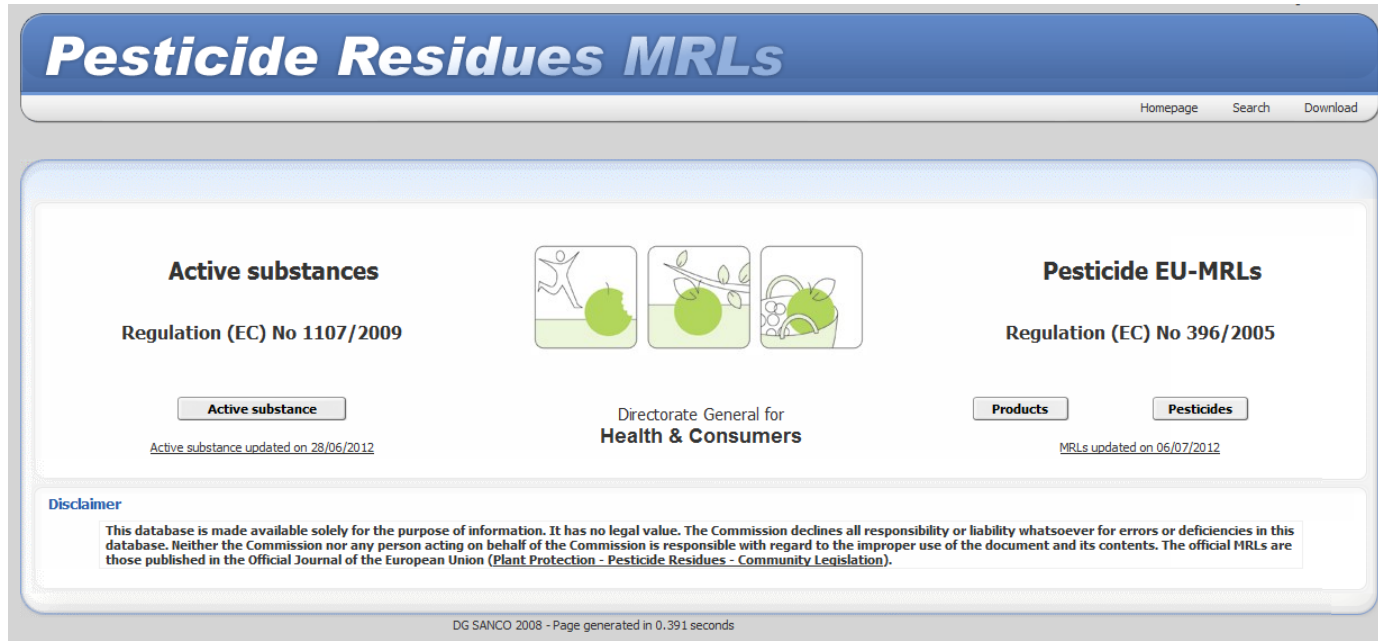
## Current Status European Review Process



The Review of existing pesticides has led to the removal from the market of pesticides which cannot be used safely. Of some 1000 active substances on the market in at least one Member State before 1993, 26 %, corresponding to about 250 substances, have passed the harmonized EU safety assessment. The majority of substances (67%) have been eliminated because dossiers were either not submitted, incomplete or withdrawn by industry. About 70 substances failed the review and have been removed from the market, because the evaluation carried out did not show safe use with respect to human health and the environment.



- 1289 substances listed
- 415 PPP approved
- 779 PPP not approved
- 75 PPP pending
- 20 not a PPP



The screenshot shows the homepage of the 'Pesticide Residues MRLs' database. The header features the title 'Pesticide Residues MRLs' and navigation links for 'Homepage', 'Search', and 'Download'. The main content area is divided into two columns. The left column is titled 'Active substances' and references 'Regulation (EC) No 1107/2009'. It includes a button labeled 'Active substance' and a note that 'Active substance updated on 28/06/2012'. The right column is titled 'Pesticide EU-MRLs' and references 'Regulation (EC) No 396/2005'. It includes buttons for 'Products' and 'Pesticides', and a note that 'MRLs updated on 06/07/2012'. In the center, there are three icons: a person with a green apple, a green apple on a branch, and a basket of green apples. Below the icons is the text 'Directorate General for Health & Consumers'. At the bottom of the page, there is a disclaimer and a footer that reads 'DG SANCO 2008 - Page generated in 0.391 seconds'.

1289 entries

514 entries

[http://ec.europa.eu/sanco\\_pesticides/public/index.cfm](http://ec.europa.eu/sanco_pesticides/public/index.cfm)



## Does the European Review Process makes global trading easier?



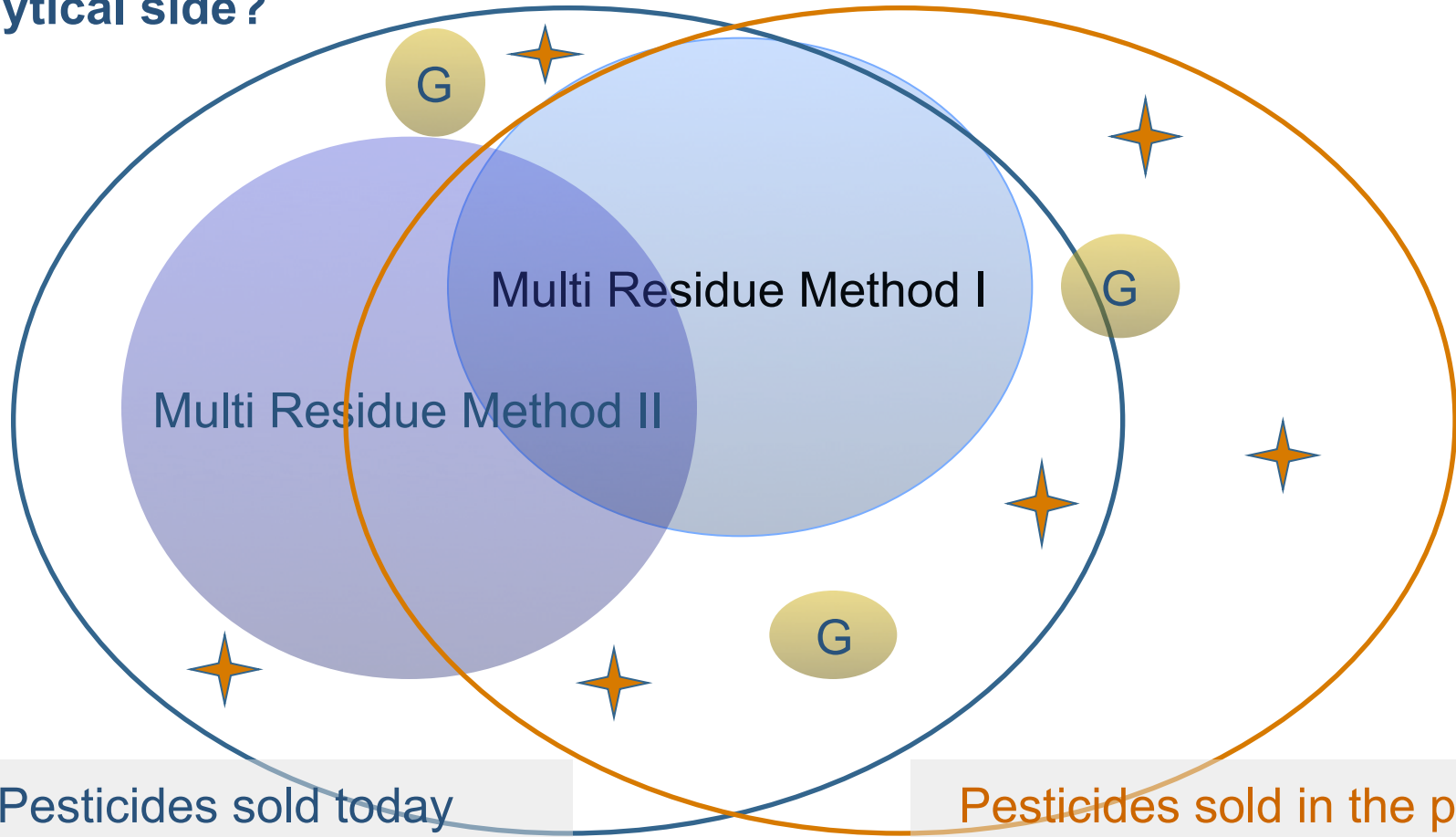
---

### Problem for EU companies importing food materials outside the EU:

- **Pesticides which are no longer approved in the EU are then normally provided with low Maximum Residue Limits (0,01mg/kg).**
- **These Pesticides are still legally used in countries outside Europe. In many cases they are also provided with comfortable MRLs by national regulations.**
- **Crops which are grown using approved agrochemicals in their countries of origin with residue levels to in accordance with their national legislation do have the permanent risk not not being in accordance with the European regulation.**

# Challenge: To find an appropriate strategy to monitor pesticide residues

How to approach these substances from the analytical side?



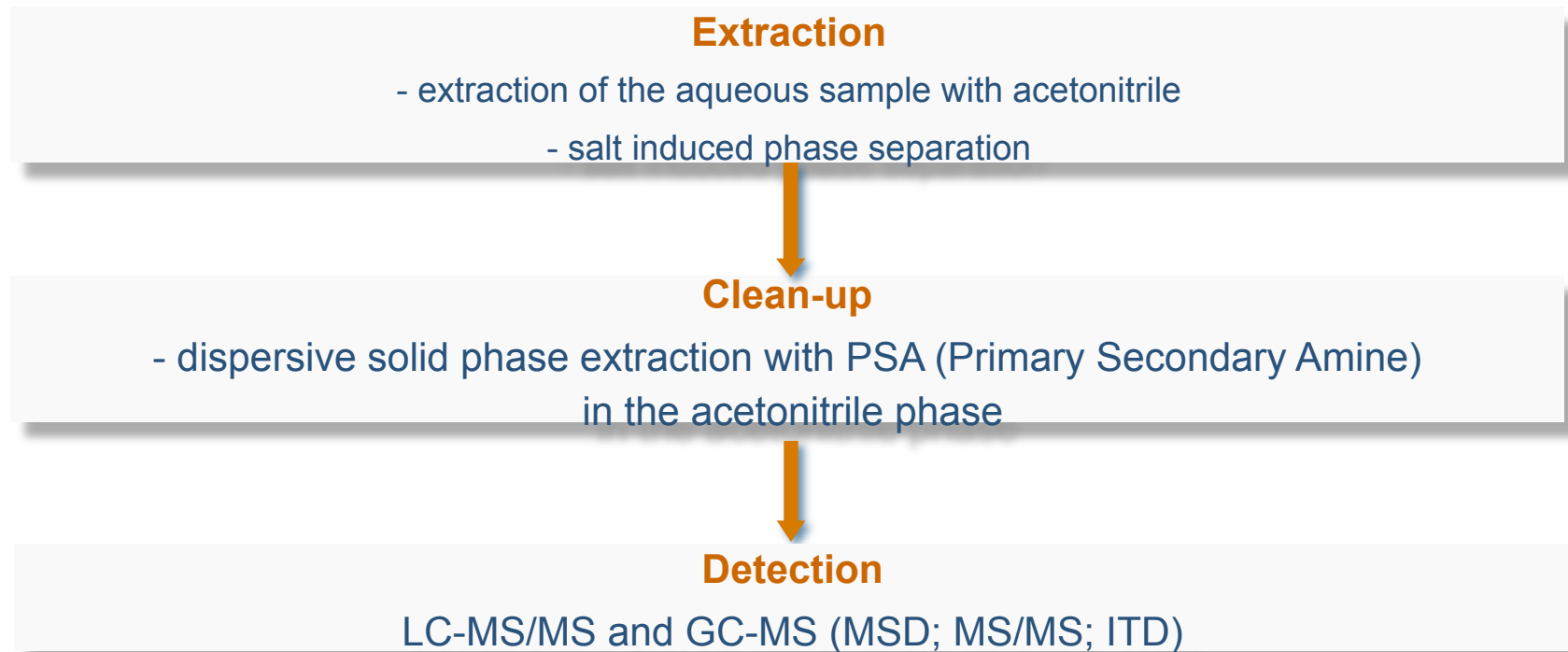
Pesticides sold today

Pesticides sold in the past

**G** Group Specific Methods

 Single Methods

QuEChERS\* = Quick, Easy, Cheap, Effective, Rugged, Safe



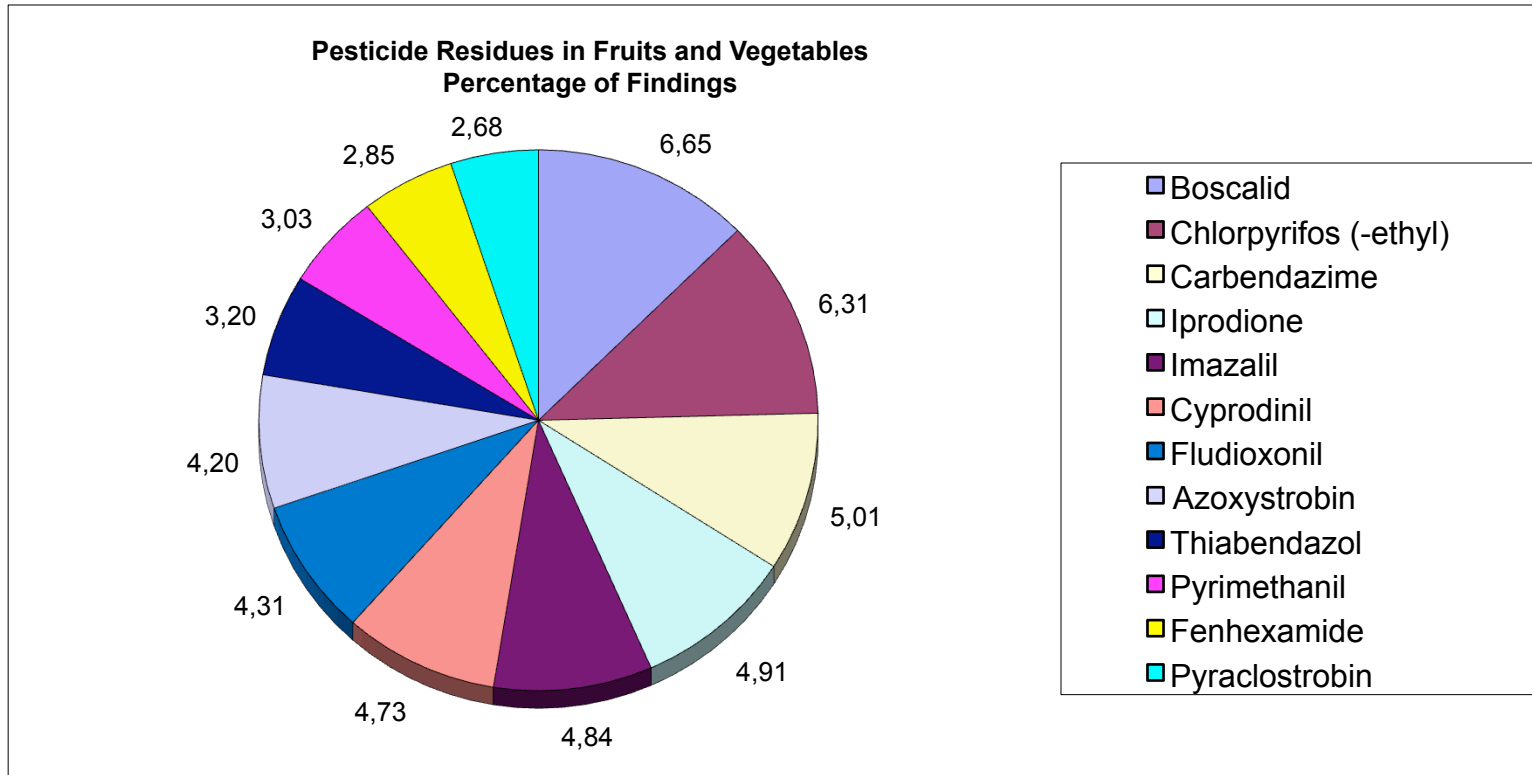
\* Anastassiades, M., S. J. Lehotay, D. Stajnbaher and F. J. Schenck (2003): "Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce." Journal of AOAC International 86(2): 412-431

## Group Specific and Single Methods

- Chlormequat / Mepiquat
- Bromide
- EDB/DBCP
- PH<sub>3</sub>
- Glyphosate / Glufosinate
- Phenylurea Herbicides
- Sulfonylurea Herbicides
- Amitraz
- Acidic Herbicides
- Dithiocarbamates
- Ethylenoxide
- Fosetyl-Al
- Maleic Hydrazide
- Organotin Compounds
- Alkanolamines and Morpholine
- Waxes
- Quaternary Ammonium Compounds (DDAC + BAC)
- Perchlorate

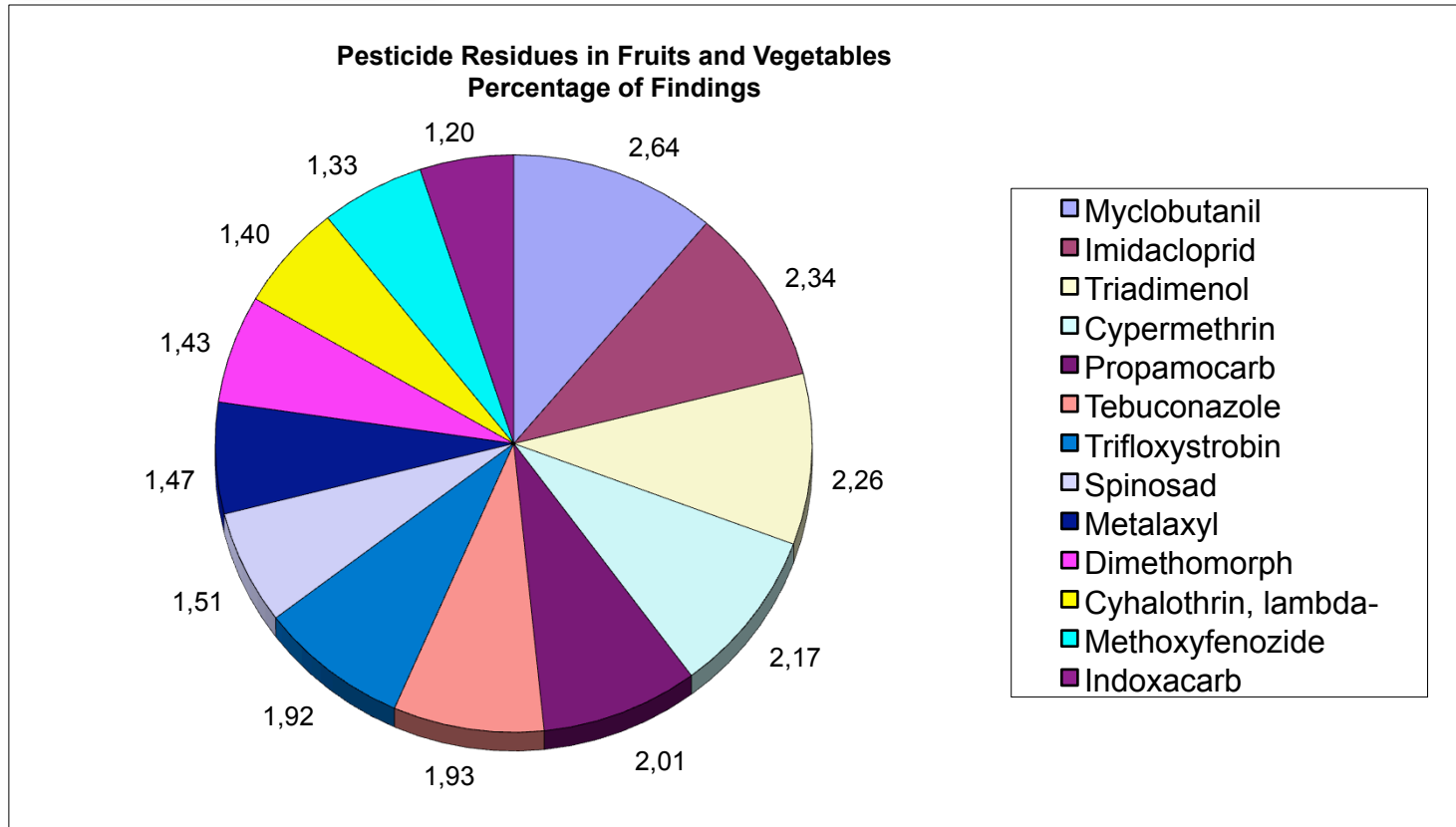


## Top 1 to 15

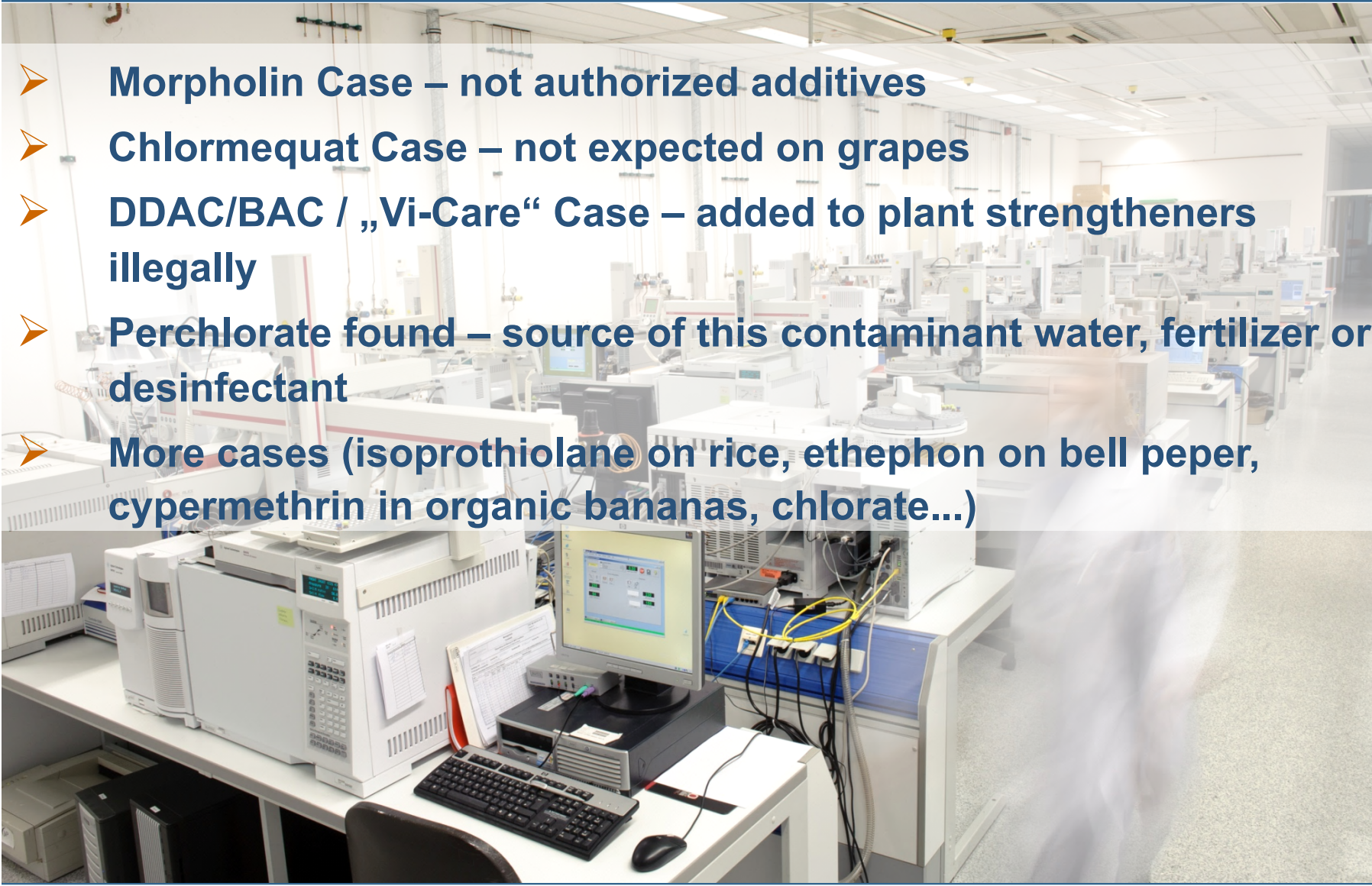


**65000 Samples analyzed between  
2010 - June 2013**

## Top 16 to 30



Out of 650 pesticides covered by the QuEChERS MRM, 200 pesticides can be concluded as relevant. (However, the pesticide at rank no. 200 (e.g. Etridiazole ) was found 10 times only! → 0,0002%)

- 
- **Morpholin Case – not authorized additives**
  - **Chlormequat Case – not expected on grapes**
  - **DDAC/BAC / „Vi-Care“ Case – added to plant strengtheners illegally**
  - **Perchlorate found – source of this contaminant water, fertilizer or disinfectant**
  - **More cases (isoprothiolane on rice, ethephon on bell pepper, cypermethrin in organic bananas, chlorate...)**

## General introduction

- Morpholine incident
  - UK authorities informed on possible presence of morpholine on waxed apples in May 2010
  - Difficulty to find lab capable of analysing substance
  - UK stakeholder consultation in September 2010
    - => unauthorised carrier used in glazing agent
    - => low risk to consumers
    - => blocking waxed apples, other waxed fruits ?





### Legal Background 2010:

Morpholine is used as a carrier, having also a function as an emulsifier, in waxes, for glazing purposes of fruits. Such use is a food additive use and Morpholine is not authorized as food additive in the EU.

Therefore this use of Morpholine is not authorized in the EU and may not be used on fruits intended to be placed on the EU market.

## Morpholine Case: Best Practice



### Best Practice:

Morpholine had been analyzed with a limit of quantification of 0.1 mg/kg.

Residue levels between 0.1 to 0.5 mg/kg: an indication for treatment may be given. However, a sample still is considered to be marketable.

Residue levels > 0.5 mg/kg: a sample has to be judged „not marketable“, additionally an identification of Morpholine in the

- surface wax of sample should be performed
- Legal Background 2012: Nothing has changed so far !
- No Changes to be expected in the near future !
- Crucial Question: which concentration on fruits is giving a clear indication for an active usage?

# Alkanolamines and Morpholine Analysis

- Morpholine (MORP)
- Diethanolamine (DEA)
- Triethanolamine (TEA)
- N,N-dimethylethanolamine (DMEA)
- N,N-diethylethanolamine (DEEA)
- 3-methoxypropylamine (MPA)
- 2-amino-2-methyl-1-propanol (AMP)

➤ ...more to come?

Sample weight: 10g  
Addition of internal standard  
Incubation for ~15min

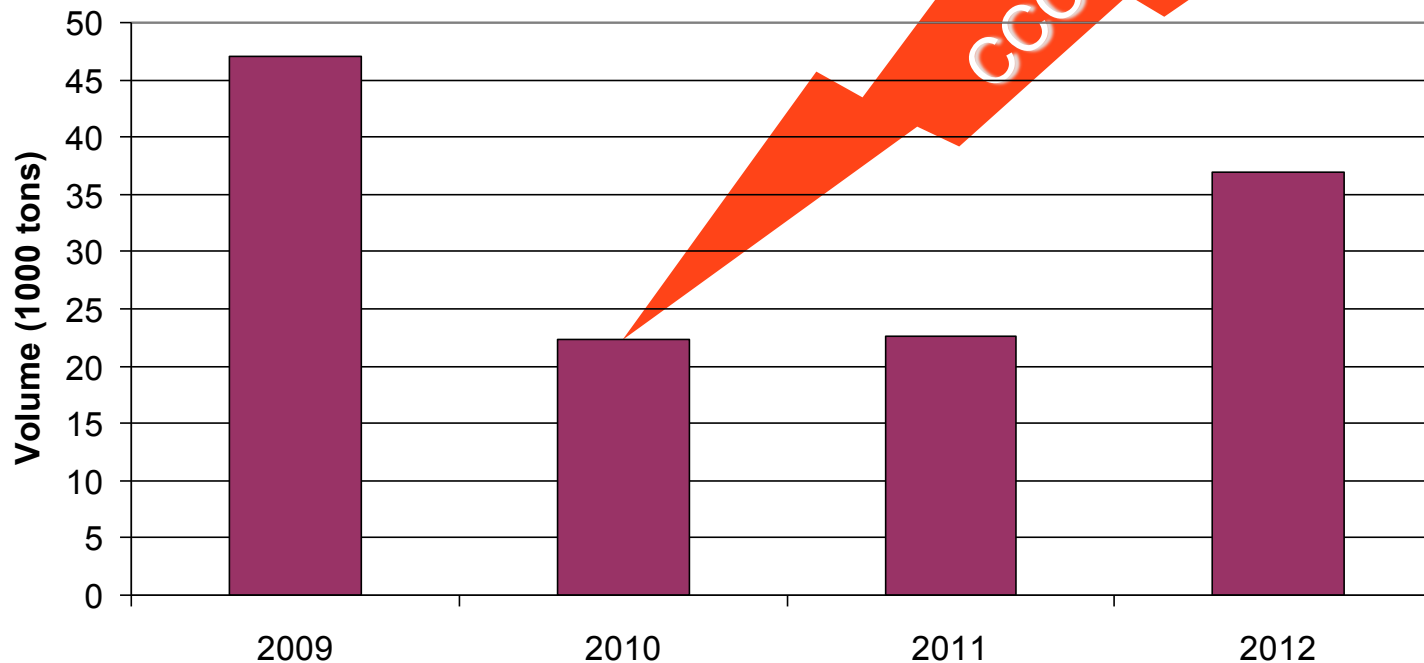
Addition of 30mL MeOH  
Vortexing for 30min  
Centrifugation for 5min at  
4000rpm

Dilution (DF=10) with ACN  
LC-MS/MS analysis



## Chlormequate Case: Indian grapes

### Export of table grapes from India to the EU



CCC is a plant growth regulator usually applied on cereal crops.

#### MRL (EU) for Chlormequat:


- Wheat: 2 mg/kg
- Grapes: 0.05 mg/kg

#### Former Chlormequat crisis:

- Pears
- Tomatoes

## EFSA evaluates Indian grapes pesticide risk

By Rory Harrington, 26-Apr-2010 MRL: 0.05 mg/kg

 1 comment

Related topics: Contamination, Quality & Safety, Cleaning / Safety / Hygiene

**An initial assessment from the European Food Safety Authority (EFSA) said current levels of the pesticide chlormequat on table grapes from India pose no threat to consumer health.**

But the food safety watchdog said the evaluation was a temporary one and that a more in-depth investigation was needed before it could deliver a definitive maximum residue level (MRL) recommendation. It did not rule out changing the "residue definition".

MRL August, 16th, 2012: 0.05 mg/kg

# Chlormequat Case:Solution

## Pre Harvest Sampling + Analysis, Full Traceability



Sampling and testing of individual fields

1 certificate for each field

The screenshot shows the Eurofins OnLine interface. The top navigation bar includes 'Accounts management', 'Results', 'Ordering services', 'Operator tools', 'Support', and 'Logout'. The main content area displays a table of samples with columns for Eurofins code, Sample description, Reception date, Sample status, Expected date of results, View results, Analytical report, and Un-viewed. An arrow points from the 'Analytical report' column to an aerial view of a field. The field view shows several red 'X' marks indicating sampling spots. Text overlays on the field view include 'Sampling spots', 'Farm Code', 'GPS coordinates: 20° 8'13.38"N X', and '74° 1'22.32"E'.

Eurofins code	Sample description	Reception date	Sample status	Expected date of results	View results	Analytical report	Un-viewed
716-2011-00001333	11-17086_EZE-MH-06-09-10-71-401	18.03.2011	Sample Validated	25.03.2011	Results Planning	AR-11-FJ-001275-01	
716-2011-00001334	11-17087_EZE-MH-06-09-11-37-901	18.03.2011	Sample Validated	25.03.2011	Results Planning	AR-11-FJ-001276-01	
716-2011-00001335	11-17593_EZE-MH-06-09-90-85-01	18.03.2011	Sample Validated	25.03.2011	Results Planning		
716-2011-00001336	11-17594_EZE-MH-06-09-14-19-602	18.03.2011	Sample Validated	25.03.2011	Results Planning		
716-2011-00001337	11-17597_AMA-MH-06-12-40-59-01	18.03.2011	Sample Validated	25.03.2011	Results Planning		
716-2011-00001338	11-17598_AMA-MH-06-12-15-484-02	18.03.2011	Sample Validated	25.03.2011	Results Planning		
716-2011-00001339	11-17620_EZE-MH-06-09-84-28-02	18.03.2011	Sample Validated	25.03.2011	Results Planning		
716-2011-00001322	11-17595_AMA-MH-06-09-14-09-301	17.03.2011	Sample Validated	24.03.2011	Results Planning		
716-2011-00001323	11-17596_AMA-MH-06-12-53-33-01	17.03.2011	Sample Validated	24.03.2011	Results Planning		
716-2011-00001324	11-17599_AMA-MH-06-09-28-97-01	17.03.2011	Sample Validated	24.03.2011	Results Planning		
716-2011-00001325	11-17600_AMA-MH-06-22-16-224-01	17.03.2011	Sample Validated	24.03.2011	Results Planning		
716-2011-00001326	11-17601_AMA-MH-06-09-14-09-201	17.03.2011	Sample Validated	24.03.2011	Results Planning		

## DDAC/BAC Case: Chronology of Events



**At this time, it turns out that 2-5% of all food on the market contain DDAC or BAC above the MRL and therefore are considered not to be marketable.**

## DDAC/BAC Case: Chronology of Events





---

**Guidelines as regards measures to be taken as regards the presence of DDAC and BAC in or on food and feed agreed by the Standing Committee of the Food Chain and Animal Health (SCoFAH) on 13<sup>th</sup> and 25<sup>th</sup> of July 2012 respectively.**

**Levels of 0.5 mg/kg are accepted.**

**Also for organic products, if a treatment as plant strengthener can be definitely excluded.**

**Member States are encouraged to take samples and collect data on that purposes in order to set an MRL by February 2013. In September 2013 an MRL of 0.1 mg/kg is discussed.**

# Quarternary Ammonium Compounds: Results

## Fresh Crops

Crop	No. of samples analyzed	No. of positiv findings	% findings in the crop
Banana	490	228	47
Parsley	54	28	52
Basil	47	24	51
Pineapple	60	19	32
Citrus	46	18	39
Rasin	35	17	49
Kiwi	55	14	25
Orange	49	14	29
Broccoli	12	9	75
Tomatoes	13	8	62
Lime	11	4	36
Grapes	15	3	20

**1385 Samples were analyzed for QAC residues:**

➤ **40% showed positive findings > 0.01 mg/kg**

## Plant Strengthenener



➤ **„Vi-care“: contained undeclared DDAC**

## Review Articles

# Perchlorate as an Environmental Contaminant

Edward Todd Urbansky

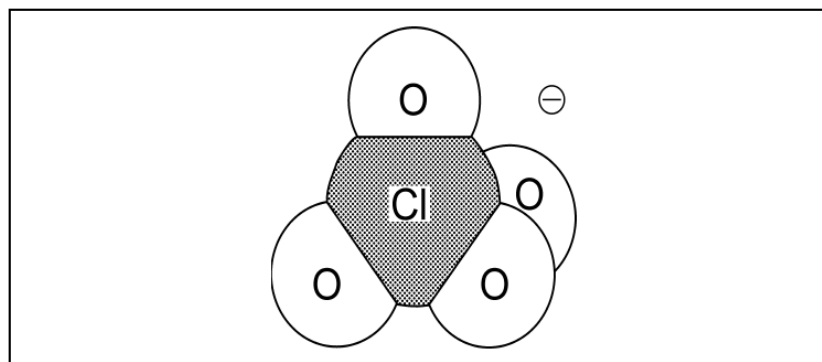
United States Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Water Supply and Water Resources Division, 26 West Martin Luther King Drive, Cincinnati, OH 45268;  
e-mail: [urbansky.edward@epa.gov](mailto:urbansky.edward@epa.gov)

DOI: <http://dx.doi.org/10.1065/espr2002.05.117>

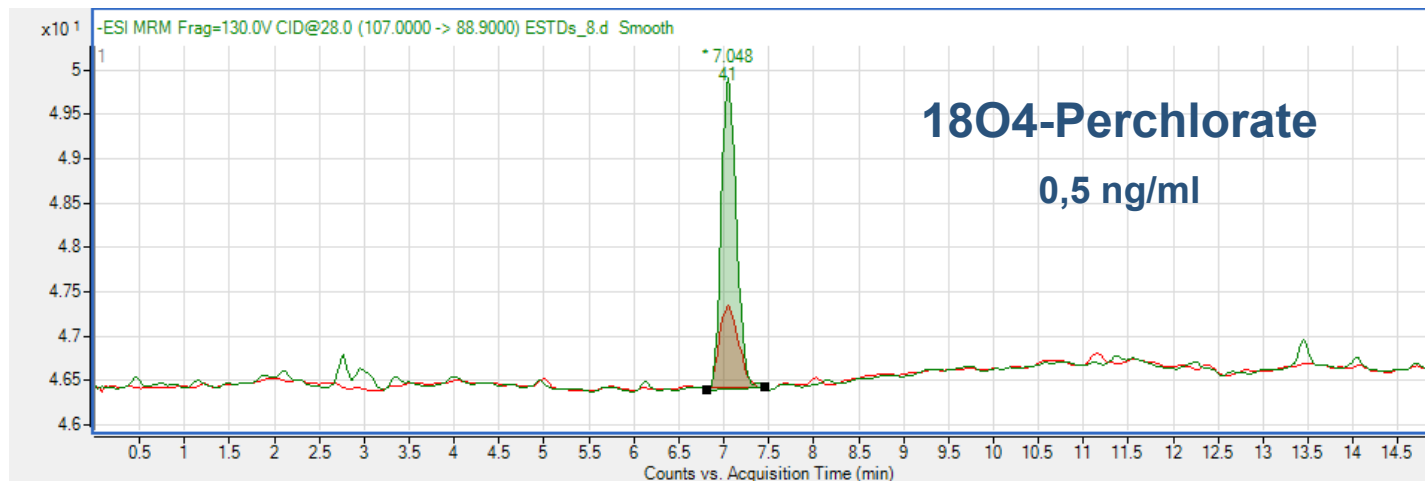
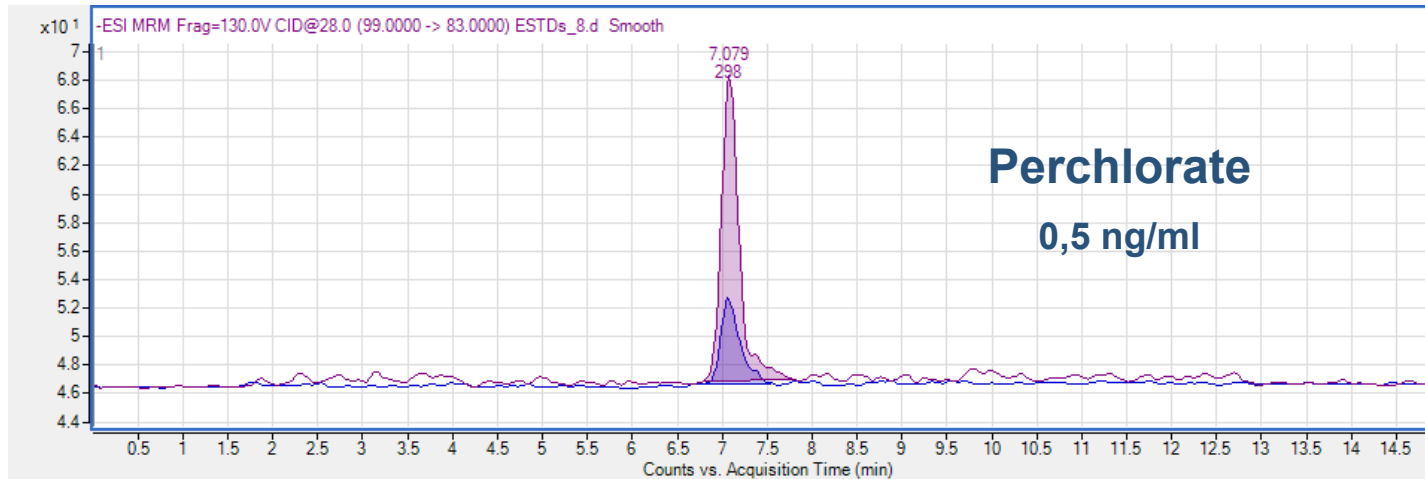
**Abstract.** Perchlorate anion ( $\text{ClO}_4^-$ ) has been found in drinking water supplies throughout the southwestern United States. It is primarily associated with releases of ammonium perchlorate by defense contractors, military operations, and aerospace programs. Ammonium perchlorate is used as a solid oxidant in missile and rocket propulsion systems. Traces of perchlorate are found in Chile saltpeter, but the use of such fertilizer has not been associated with large scale contamination. Although it is a strong oxidant, perchlorate anion is very persistent in the environment due to the high activation energy associated with its reduction. At high enough concentrations, perchlorate can affect thyroid gland functions, where it is mistakenly taken up in place of iodide. A safe daily exposure has not yet been set, but is

## 1 General Chemistry

The perchlorate anion ( $\text{ClO}_4^-$ ) consists of a tetrahedral array of oxygen atoms around a central chlorine atom (Fig. 1).

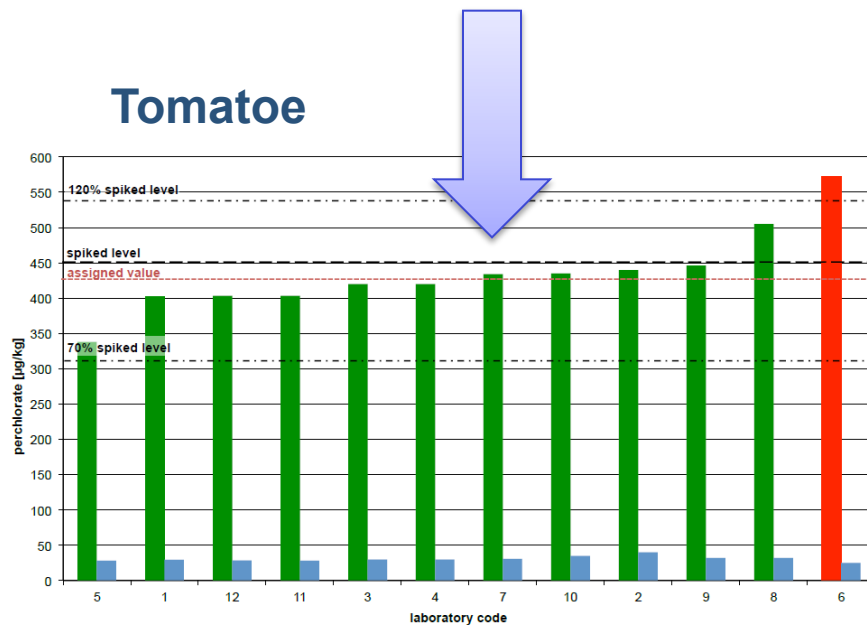


## Typical Chromatograms

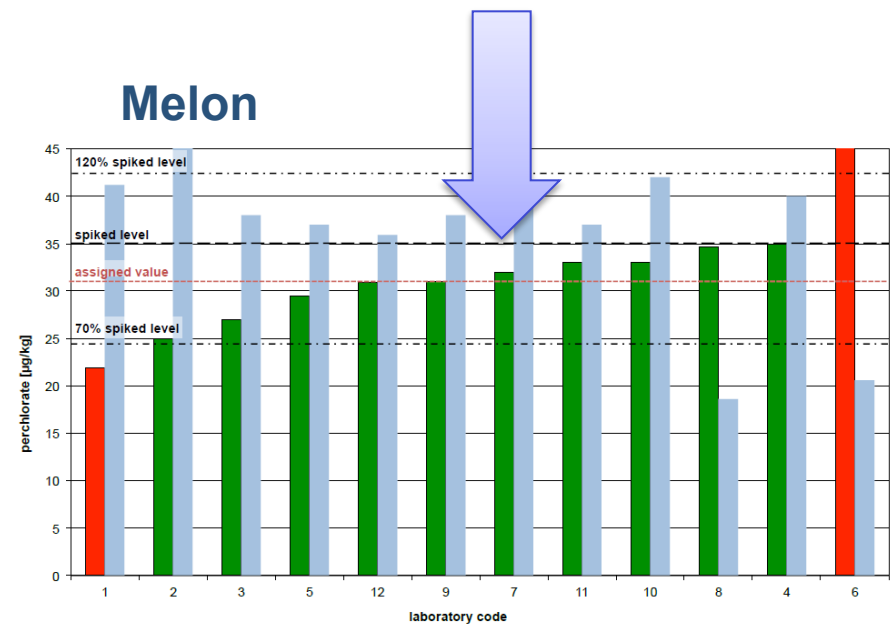


➤ 4.6.2013: Ringtest – Perchlorat

➤ Successfully passed



green: satisfactory results, red: non satisfactory results, blue: results from Blank Material



green: satisfactory results, red: non satisfactory results, blue: results from Blank Material

# Solution – action limits



**NL: Signalwerteliste (03.05.13)**

Erzeugnis	product	EC code	Actionlimit
Ananas	Pineapples	163080	0,49
Äpfel	Apples	130010	0,28
Aprikosen	Apricots	140010	0,81
Artischocken	Globe artichokes	270050	3,0
Auberginen	Aubergines	231030	1,3
Avocado	Avocados	163010	2,1
Azarole	Azarole (medjool)	154070	8,0
Bambunssprosser	Bamboo shoots	270080	7,7
Bananen	Bananas	163020	0,49
Basilikum	Basil	256080	15
Birnen	Pears	130020	0,31
Blumenkohl	Cauliflower	241020	0,72
Bohne (mit Hülse)	Beans (with husk)	260010	0,80
Bohne (ohne Hülse)	Beans (without husk)	260020	1,4
Bohnen	Beans	300010	0,55
Broccoli	Broccoli	241010	0,63
Brombeeren	Blackberries	153010	0,93
Brunnenkresse	Water cress	254010	8,5
Cherimoya	Cherimoya	163060	3,3
Chicoree	Witloof	255000	0,6
Chinakohl	Chinese cabbage	243010	1,3
Cranbeeren	Cranberries	154020	2,2
Datteln	Dates	161010	3,2

**Labore\_De: Signalwerteliste (29.04.13)**

Signalwert	Erzeugnis	Anmerkung
0,22	Ananas	Fruchtfleisch
0,12	Äpfel	
0,33	Aprikosen	
0,34	Auberginen	Wert für verarbeitete Auberginen angenommen
0,30	Avocados	Fruchtfleisch (VF=7)
0,18	Bananen	Fruchtfleisch
0,11	Birnen	
1,5	Grüne Bohnen	
0,42	Chinakohl	Wert für verarbeiteten Chinakohl angenommen

### ➤ StALut/BMELV (German authorities) Juli 2013

SEITE 2 VON 3

Sehr geehrte Damen und Herren,

bekanntlich sind in jüngerer Zeit vor allem in Obst und Gemüse teilweise erhöhte Gehalte an Perchlorat nachgewiesen worden. Um ein einheitliches Vorgehen innerhalb der EU in die Wege zu leiten, ist am 16. Juli 2013 im Ständigen Ausschuss die anliegende Erklärung zum weiteren Vorgehen hinsichtlich des Auftretens von Perchlorat in Lebensmitteln wie insbesondere Obst und Gemüse angenommen worden.

Als Referenzwerte für den innergemeinschaftlichen Handel sollen gelten:

Alle Lebensmittel / Obst und Gemüse	0,5 mg/kg
mit Ausnahme von	
• Zitrusfrüchten, Kernobst, Wurzel- und Knollengemüse, Tafeltrauben, Spinat, Melonen und Wassermelonen	0,2 mg/kg
• Blattgemüse (außer Spinat), frische Kräuter und Sellerie aus Gewächshäusern und Anbau unter Folie	1,0 mg/kg

Diese Werte sollen vorübergehend zur Anwendung kommen, bis die Risikobewertung der Europäischen Behörde für Lebensmittelsicherheit (EFSA) vorliegt. Letztere wird Ende diesen Jahres erwartet.

### ***Bewertung der Rückstände von Perchlorat:***

***In der vorliegenden Probe wurde Perchlorat in einer Konzentration von x mg/kg nachgewiesen.***

***Die möglichen Eintragsquellen für Perchlorat sind unterschiedlich und nach derzeitigem Kenntnisstand noch nicht eindeutig identifiziert. Natürliche Quellen wie Trinkwasser oder Dünger sind ebenso diskutiert wie ein Eintrag als Nebenprodukt aus der Desinfektion bspw. von Wasser mit chlorhaltigen Mitteln.***

***Perchlorat unterliegt weder einer Einstufung als Pflanzenschutzmittel noch als Biozid und ist derzeit als Kontaminante im Sinne der Verordnung EG/315/93 zu beurteilen.***

***Nach Artikel 2 Abs 1 der o.g Verordnung darf kein Lebensmittel in den Verkehr gebracht werden, das eine Kontaminante in einer gesundheitlich und insbesondere toxikologisch nicht vertretbaren Menge enthält.***

***Gemäß Artikel 2 Abs 2 der Verordnung EG/315/93 sind die Kontaminanten darüber hinaus auf so niedrige Mengen wie möglich zu reduzieren, wie sie durch gute Praxis erreicht werden können.***



Home | Video | Themen | Forum | English | DER SPIEGEL | SPIEGEL TV | Abo | Shop | Schlagzeilen | Wetter | TV-Programm | mehr

**SPIEGEL ONLINE WIRTSCHAFT**

Abo | Shop | E-Paper | E-Books | Audio | Newsletter | Archiv | Spiele | Blogs

**ZEIT ONLINE | GESUNDHEIT**

STARTSEITE POLITIK WIRTSCHAFT MEINUNG GESELLSCHAFT KUNST

Gesundheit | Umwelt | Geschichte

**LEBENSMITTEL**

## Obst und Gemüse chemisch

Ob vom Discounter oder vom Markt: In zwei von drei Lebensmitteln haben Experten die Substanz Perchlorat gefunden. Sie wird in Schilddrüsenmedikamenten eingesetzt.



Gemüse auf dem Wochenmarkt: Waschen hilft nicht gegen Perchlorat

Hamburg - Obst und Gemüse vom Discounter, Supermarkt und Wochenmarkt können nach [Recherchen des NDR-Magazins "Markt"](#) mit der Chemikalie Perchlorat kontaminiert sein.

**Bild.de** FINDEN

BILD MOVIES | THEMEN | BILD MOBIL | WETTER | BILD-SHOP

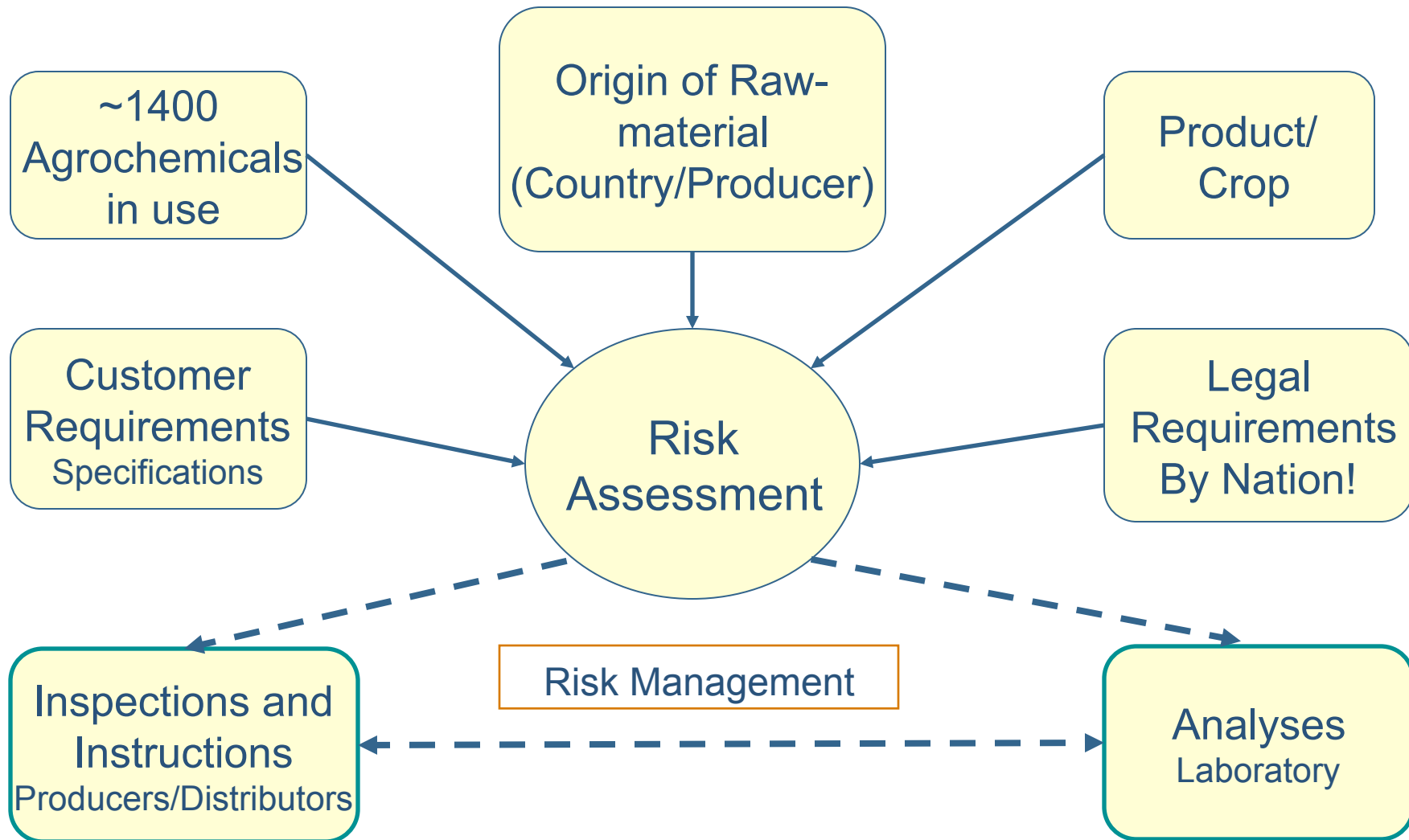
HOME NEWS POLITIK GELD SHOW SPORT LIFESTYLE **RATGEBER** REISE AUTO DIGITAL SPIEL

Home » Ratgeber » Verbrauchertipps » Gemüse » Perchlorat im Obst und Gemüse! Das Mittel steckt auch in Raketentreibstoff

### DAS MITTEL STECKT AUCH IN RAKETENTREIBSTOFF

## Perchlorat im Obst und Gemüse!

## Conclusion: Risk Assessment



## Conclusion: Requirements to Producers and Suppliers



### Producer / Farmer

- Agrochemicals / Formulations
- Plant Strengtheners
- Impact from neighbourhood fields
- Environment: Soil, Water, Air
- Desinfectants in ware houses and packing stations
- Washing agents
- Packaging materials

### Supplier (Packer/Distributor)

- Consignee
  - Specification / Secondary Standard
    - Max. MRL-Ratio
    - Max. ARfD-Ratio
    - Max. No. of Pesticides per product
    - Negative Lists / Banned Pesticides
    - Approved Pesticide
- Recipient Country – MRL Regulation
- Desinfectants in ware houses and packing stations
- Washing agents
- Packaging materials

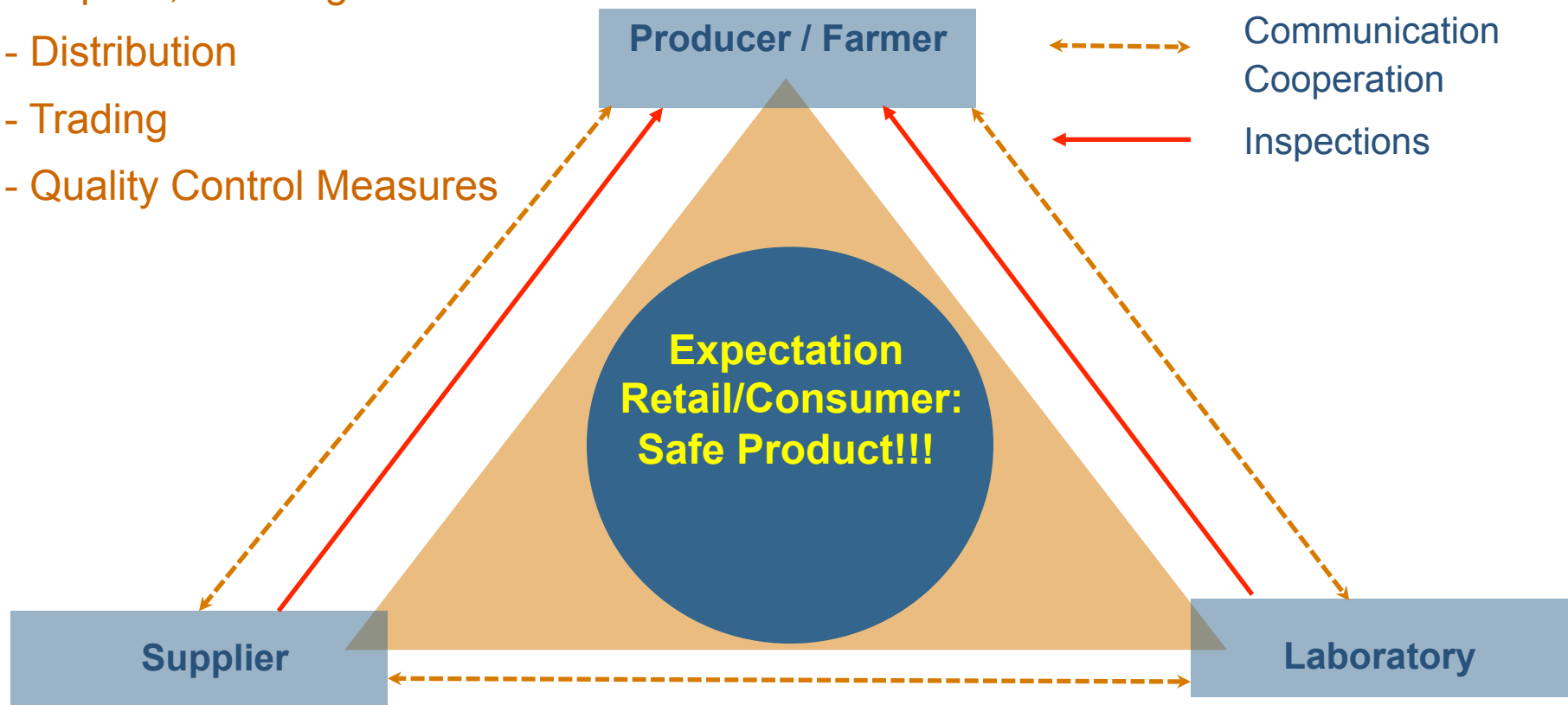
➔ Less agrochemicals, more additives and contaminants

➔ watch microbiological issues !

## Conclusion: Triangle of Responsibilities

Stakeholders involved in:

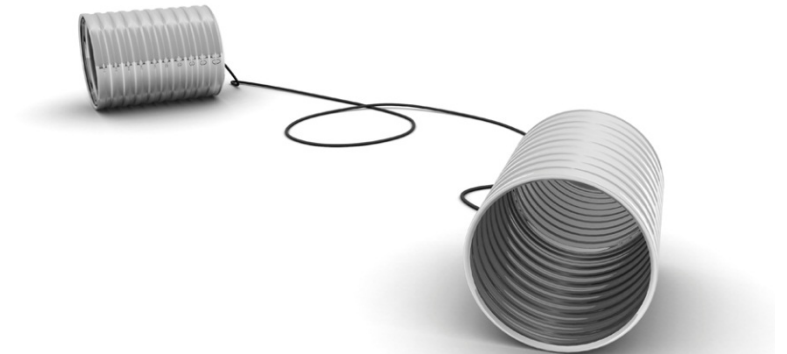
- Production
- re-pack, handling
- Distribution
- Trading
- Quality Control Measures



**Thank you very much!**

**Muchas gracias!**

**For further details or questions, please  
feel free to ask!**



Contact:

Eurofins Food | Dr. Specht  
Laboratorien

Grossmoorbogen 25, 21079 Hamburg,  
Germany

Fon: +49-(0)40-881 448-0

[thiesclaussen@eurofins.de](mailto:thiesclaussen@eurofins.de)

[www.eurofins.de](http://www.eurofins.de)