

# Managing residues and MRL's

## Welcome

Green Agro Control  
ISO 17025

TomatoesNZ

Delft Research Group

- Green Agro Control
  - Laboratory
    - Fertilizers
    - Pesticides
    - Chemicals specific
  - Research
    - Diagnosics
    - Monitoring
    - Laboratory
    - Practice
- FytoConsult AP
  - Crop advice
  - Integrated Pest Management
- Agro Expertiseburo
  - Expertise
  - Legal support

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Groen Agro Control  
28 July 2015

# Pesticide are organic chemicals

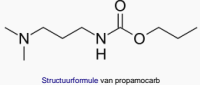
- Seems like 'all natural' because it breaks down to CO<sub>2</sub> H<sub>2</sub>O O<sub>2</sub> N<sub>2</sub>
- While nutrients inorganic chemicals

But it is (see also IUPAC)

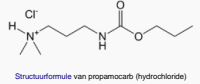
- This is Previcur N
- Propamocarb hydrochlorine
- Soil degradation (aerobic) DT50 14 days
- Water DT50: not known

**Propamocarb**

Structuurformule en molecuulmodel



Structuurformule van propamocarb



Structuurformule van propamocarb (hydrochloride)

**Algemeen**

Molecuulformule C<sub>14</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub> (zout)

IUPAC-naam propyl-3-(dimethylamino)propylcarbamate

# Pesticides Residue

- Multi residue screening > 600 components 0.01 mg/kg
- Accredited ! (e.g. ISO17025)
- Service on EU-MRL and Retail demands (%MRL, Arfd)
- Decline studies in crop
- Consultancy: on treatments, risk analysis, monitoring Global GAP

Note that MRL = result of concentration after effective treatment (dosis + PHI) and NOT a human safety concentrations. For that other studies are done+Arfd

# Pesticides method

**Selectivity:** Identification and validation of component between all other organic components + plant material

**LOD:** limit of detection, EU = reporting limit 0,01 **mg/kg**. When no EU-MRL specific than default is <0,01

- GC-MS (0,01) - GC-MSMS (0,003) - LC-MSMS 0,01
- BabyFood LC 0,002 - Water 0,02 **ug/liter (1000x lower)**

**Development:** Report on same day of sampling, >>600 components, Finding a solution at recall

**Dutch reference laboratory**

# Agro specific measurements

Related to plant damage

In air: Ethylene, CO. In water: O<sub>2</sub>, Fluoride, fire retardants, plasticizers  
Herbicide: list of 200 components

Damage cases:

- Expertise and tests- Minimise damage
- Trials in greenhouse to proof that damage is caused by.... e.g.2,4D

Content of fruit vegetables

Nutritional value, Sugars, Vitamins, Amino acids, Health promoting components (Lycopene in tomato, or selenium in cansicum)

Tube for taking gas-sample

# Residue: EU-MRL's

MRL are all the "same" in European Union on (EG396/2005) for pesticides

Open website (google EU MRL) gives [http://ec.europa.eu/sanco\\_pesticides/public/?event=homepage&language=EN](http://ec.europa.eu/sanco_pesticides/public/?event=homepage&language=EN)

e.g. Grapefruit

Pesticide Residue	Maximum residue level (mg/kg)
1	
1,1-dichloro-2,2-bis(4-ethylphenyl)ethane (F)	0.01*
1,2-dibromoethane (ethylene dibromide) (F)	0.01*
1,2-dichloroethane (ethylene dichloride) (F)	0.01*



## Deviations in samples

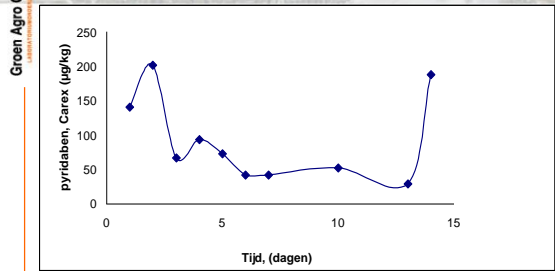
Sample: e.g. tomato, random taken, 10 pieces and/or 1kg, harvest ripe / yielded product

### Differences

- Path: because of distance spray equipment - fruit
- Front or back of the fruit
- Position on truss (covered by big ones)
- Stage of growth

Sampling is very important

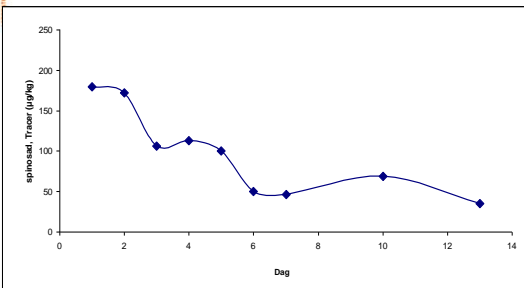
## Treatment in tomato: decline in time



"Practical" treatment: by "fogging" all together on day 0  
 Pyradaben, Carex: 1 liter/ha (and day 13, 1 liter/ha)  
 Spinosat, Tracer: 0.5 liter/ha  
 Fenhexamide, Teldor: 1.5 kg/ha

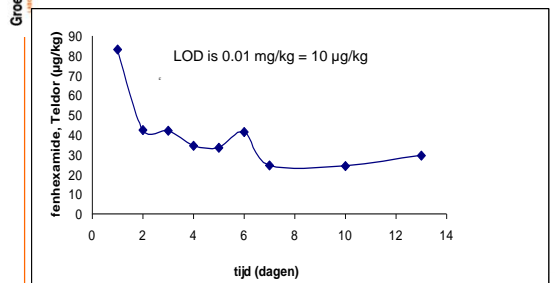
## Decline

Spinosat, Tracer, 0,5 liter/ha -> 220 ug/kg fresh tomato



## Decline

Fenhexamide, Teldor 1,5 kg/ha -> 85 ug/kg fresh tomato



## Decline

Tomaat v 1tros	%Teldor	%Carex	%Tracer
tros 4 tomaat 1	100%	100%	100%
tros 4 tomaat 2	164%	222%	177%
tros 4 tomaat 3	105%	161%	147%
tros 4 tomaat 4	107%	280%	225%
tros 4 tomaat 5	86%	140%	161%

1 tomato: 86-280% residu difference on cluster tomatoes

Path number after fogging every 10th row, is very relevant for concentration

PadNr	Fog=0	% Teldor	% Carex	% Tracer
0		100%	100%	100%
3		21%	19%	20%
6		9%	9%	10%
9		5%	5%	8%

## Conclusion treatment


- It takes long before <0.01 mg/kg
- Be aware of the variation between samples
- Method of treatment -> other concentration
- Good and well cared equipment
- Variation between fruits can differ a lot

Contra sample can differ 50% than the earlier measured concentration

## Residues are the responsibility of the whole chain

Soil/substrate to grow on  
 Production on the field  
 -Crop protection  
 -IPM  
 -Neighbour crop  
 -Fresh (?) water  
 -Dung of animal/bird

People (personal hygiene)  
 Sorting (cleaning product)  
 Packaging (ink, plasticizer)  
 After yield treatment (UV, ozon, ionisation)  
 Storage (rot, mycotoxins)  
 Transport (gasses)



## THE END



Thank you for your attention  
 Ines van Marrewijk

## (Per)Chlorat: where does it come from

Perchlorate (0.1 MRL Tomato) Perchlorate -> harmful to function of thyroid (contamination)






- Soil -> water (tap water US)
- Inorganic Fertilizers: most in Potassiumnitrate (KNO<sub>3</sub>), Sulfates, Phosphates
- Guano and other organic manure

Chlorate (0.25 MRL Tomato) Not in legislation (but is old herbicide)

- Most from chloride in biocide given in drip-water
- Degradation product from Sodium Hypochlorite, ECA, ClO<sub>2</sub>
- Known as an old herbicide: so still in soil
- From fertilizers? not known

## Chloride -> to PerChlorate Oxidation states

- Chloride Cl<sup>-</sup>
  - Oxidizer of organic matter, micro-organism, fungi and bacteria
- Hypochlorite; ClO<sup>-</sup>
- Chlorite; ClO<sub>2</sub><sup>-</sup>
- Chlorate; ClO<sub>3</sub><sup>-</sup>
- PerChlorate; ClO<sub>4</sub><sup>-</sup>

Chlorine oxidation state	-1	+1	+3	+5	+7
Name	chloride	hypochlorite	chlorite	chlorate	perchlorate
Formula	Cl <sup>-</sup>	ClO <sup>-</sup>	ClO <sub>2</sub> <sup>-</sup>	ClO <sub>3</sub> <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>
Structure					

## Microbiological analysis in Food

EG2073 Microbiological criteria in Food

Therefore we developed our accredited methods

- Total plate Count - E. coli (EHEC)
- Enterobacteriaceae - Yeast and Moulds
- Listeria monocytogenes - Salmonella spp
- Campylobacter jejuni - Bacillus cereus
- Vibrio spp - Norovirus
- Staphylococcus aureus - Alicyclobacillus
- Lactic acid Bacteria

Samples is mostly fresh product but also on location:

- Air-samples, Swabs, and plates for own sampling of hygiene or human pathogens