



Risikovurdering vedr. chlorpyrifos og chlorpyrifos-methyl - Forarbejdede fødevarer og animalske fødevarer

Jensen, Bodil Hamborg; Nielsen, Elsa Ebbesen

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NOTAT

Til Fødearestyrelsen

Vedr. Risikovurdering vedr. chlorpyrifos og chlorpyrifos-methyl -
Forarbejdede fødevarer og animalske fødevarer

Fra Fødevareinstituttet DTU

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Risikovurdering vedr. chlorpyrifos og chlorpyrifos-methyl - Forarbejdede fødevarer og animalske fødevarer

Forespørgsel

1. Kan det udgøre en risiko for forbrugerne at indtage et animalsk produkt (alle relevante dyrearter), hvis der er chlorpyrifos i foderet?
2. Bliver chlorpyrifos og chlorpyrifos-methyl nedbrudt, når fødevarer forarbejdes?

Konklusion

1. Da et genotoksisk potentiale ikke kan afklares for chlorpyrifos og chlorpyrifos-methyl, og da det antages, at der ikke er en nedre tærskel for eventuelle genotoksiske effekter, vurderes det, at en sundhedsmæssig risiko ikke kan udelukkes ved indtag af et animalsk produkt, der kan indeholde chlorpyrifos eller chlorpyrifos-methyl via indtag af stoffet i foderet.
2. Chlorpyrifos nedbrydes under hydrolytiske betingelser som pasteurisering, bagning/kogning og sterilisation hovedsagelig til metabolitten TCP med metabolitten desethyl chlorpyrifos (DES) som en signifikant intermediate under sterilisation. Der er fastsat forarbejdnings faktorer for forskellige afgrøder.

Chlorpyrifos-methyl nedbrydes under forarbejdning som pasteurisering, bagning/kogning og sterilisation hovedsagelig til metabolitten desmethyl chlorpyrifos-methyl (DEM) (21.5-90.7%) afhængig af processen. Dannelsen af metabolitten er stigende med temperaturen, idet 25% dannes under pasteurisering, 80% dannes under kogning/bagning og næsten 100% nedbrydes hertil under sterilisation. Ligeledes dannes metabolitten TCP i mængde mellem 2.1-7.7%. Der er fastsat forarbejdningsfaktorer for forskellige afgrøder.

Vurdering

1. Kan det udgøre en risiko for forbrugerne at indtage et animalsk produkt (alle relevante dyrearter), hvis der er chlorpyrifos og chlorpyrifos-methyl i foderet?

Der er godkendte brug i bl.a. citrusfrugter og oliefrø for chlorpyrifos og chlorpyrifos-methyl, der kan bruges til fodring. Ved fastsættelse af MRLer i animalske produkter, er der på baggrund af restindhold for de afgrøder, der kan bruges til fodring beregnet et indtag for dyr. Det beregnede indtag er herefter sammenholdt med fodringsforsøg, og på denne baggrund er der fastsat MRLer i animalske produkter. Dvs. hvis foder indeholder chlorpyrifos eller chlorpyrifos-methyl i tilstrækkelig mængde, kan det resultere i restindhold i animalske produkter.

Da et genotoksisk potentiale ikke kan afklares for chlorpyrifos og chlorpyrifos-methyl, og da det antages at der ikke er en nedre tærskel for eventuelle genotoksiske effekter, vurderes det, at en sundhedsmæssig risiko ikke kan udelukkes ved indtag af et animalsk produkt, der kan indeholde chlorpyrifos eller chlorpyrifos-methyl via indtag af stoffet i foderet.

2. Bliver chlorpyrifos og chlorpyrifos-methyl nedbrudt, når fødevarer forarbejdes?

Chlorpyrifos

I en EFSA opinion fra 2012 angives der under “*Effect of industrial processing and/or household preparation*”:

Studies investigating the nature of chlorpyrifos residues in processed commodities were assessed in the peer review and showed that the compound progressively degrades to 3,5,6-trichloropyridinol (TCP) under the processing conditions representative for pasteurization, boiling/cooking and sterilization. Several processing studies were provided and the data were sufficient to derive the following processing factors, which are recommended to be included in Annex VI of Regulation (EC) No 396/2005:

Citrus, peeled: < 0.03	Barley, beer: <0.1
Banana, peeled: 0.02	Barley, brewing malt: 0.36
Grape, wine: <0.2	Wheat, bran: 3.38
Grapes, dry pomace: 8.74	Wheat, white flour: 0.38
Tomato, juice: <0.04	Wheat, white bread: 0.34
Tomato, puree: <0.06	Wheat, wholemeal flour: 1.31
Tomato, canned: <0.04	Wheat, wholemeal bread: 0.72

The nature of chlorpyrifos residues after processing was investigated in studies performed at three test conditions representing pasteurization, baking/brewing/boiling and sterilization (20 minutes at 90C, pH 4; 60 minutes at 100C pH 5; 20 minutes at 120C, pH 6) during the peer review (Spain, 2003). Under the representative processing conditions the compound was almost completely degraded to TCP with desethyl chlorpyrifos (DES) as a significant intermediate under the sterilisation conditions. The studies demonstrated that for processed commodities the residue definition for risk assessment shall take into account the occurrence of the metabolite TCP (Spain, 2003).

Regarding the magnitude of residues, specific processing studies were submitted by the applicant in the framework of the MRL applications (Spain, 2010a; 2010b). The samples for processing were taken from the supervised residue trials and analysed for chlorpyrifos and its metabolites TCP. In the studies on grapes, both red (two studies) and white (one study) grapes were processed into wine. For the calculation of the processing and conversion factors, the LOQ value of 0.01 mg/kg was used when the residues were recorded as below the individual LOD of the analytical methods. Since no significant residues occurred in the raw agricultural commodity (\leq LOQ), no processing studies are required for rape seeds, maize and sugar beets (EC, 1997d).

En oversigt over indholdene af chlorpyrifos og TCP i forskellige forarbejdede afgrøder gives i nedenstående tabel

Processed commodity	Number of studies	Median PF ^(a)	Median CF ^(b)	Individual PF	
				Chlorpyrifos (CHP)	Total TCP, as CHP equivalents
Enforcement residue definition: chlorpyrifos					
citrus, peeled	12	< 0.03	n.a.	Residues in the edible portion: Oranges: 5 x <0.01; 0.012 mg/kg Mandarins: 6 x <0.01 mg/kg	
Banana, peeled	5	0.02	n.a.	<0.007; <0.02; 0.02; 0.09; 0.13 mg/kg	
Orange, juice	1	Processing factors cannot be recommended for enforcement purposes as only one or two studies are available for each type of processing.		Residue in the processed product:	
Orange, essential oil	1			0.03 mg/kg	0.04 mg/kg
Apple, juice	1			<0.01 mg/kg	<0.02 mg/kg
Apple, puree	1			<0.01 mg/kg	<0.02 mg/kg
Apple, dry pomace	1			2.92 mg/kg	3.39 mg/kg
Grapes, raisin	2			0.17; 0.95	0.77; 0.87
Grapes, must	3			0.39	2.0
Grapes, dry pomace	3	8.74	1.66	4.28; 8.74 ^(c) ; 19.26	3.37; 6.81 ^(c) ; 10.53
Grapes, wine at bottling	3	<0.2	2.0	<0.2; <0.19 ^(d) ; <0.32	0.17; 0.26; 0.33 ^(d)
Grapes, wine at 6 months after bottling	3	<0.2	2.0	<0.2; <0.19 ^(d) ; <0.32	0.17; 0.26; 0.42 ^(d)

a) Median processing factor obtained by calculating the median of the individual processing factors of each processing study according to the enforcement residue definition.

b): Median conversion factor for enforcement to risk assessment obtained by calculating the median of the individual conversion factors, which expresses the ratio between the residue level in the processed commodity according to the residue definition for risk assessment and the residue level in the processed commodity according to the residue definition for enforcement. For risk assessment purpose, the amounts

of total TCP were converted into chlorpyrifos equivalents by using a conversion factor of 1.77, based on the molecular weight ratio.

(c) Two methods of wine processing were used to produce the process fractions, heating and maceration.

The result represents the mean of the two values obtained after the use of the two different methods

Metabolitten TCP dannes under hydrolytiske betingelser som pasteurisering, bagning/kogning og sterilisation. Ved sterilisation dannes endvidere metabolitten desethyl-chlorpyrifos.

Det er i en EFSA opinion fra 2012 samt i opinion fra 2014 vurderet, at der kan bruges en ADI på 0,03 mg/kg lgv/dag og en ARfD på 0,25 mg/kg lgv/dag i risikovurderingen af TCP.

I EFSA 2014 nævnes endvidere, at der kræves en ny standard hydrolyse undersøgelse til at vurdere om metabolitten desethyl-chlorpyrifos skal med i restdefinitionen for risikovurdering for forarbejdede afgrøder. De toksikologiske egenskaber for denne metabolit er endvidere ikke afklaret.

I BRF's database over processing faktorer findes der ligeledes en oversigt over processing faktorer for forskellige afgrøder. Denne kan ses via følgende link

<https://mobil.bfr.bund.de/cm/349/bfr-data-compilation-on-processing-factors.pdf>

Chlorpyrifos-methyl

For chlorpyrifos-methyl angives det i EFSA's konklusion (EFSA 2017) for art. 12 review af chlorpyrifos-methyl:

A study investigating the effect of processing on the nature of residues was provided to the RMS in the active substance renewal dossier. This study has been evaluated by the RMS and is therefore considered in the framework of the present review (Spain, 2016b). It covers the representative hydrolytic conditions for pasteurisation (20 min at 90°C, pH 4), boiling/brewing/baking (60 min at 100°C, pH 5) and sterilisation (20 min at 120°C, pH 6). This study clearly demonstrates that chlorpyrifos-methyl readily degraded when subject to hydrolytic conditions. The level of degradation increases with temperature: 25% degradation under pasteurisation, 80% degradation under boiling/brewing/baking and almost 100% degradation under sterilisation. The main degradation product is desmethyl chlorpyrifos-methyl (DEM) (21.5–90.7% of the applied radioactivity (AR)) which was already observed in cereal grain (see Section 1.1.1). The metabolite 3,5,6-TCP is also observed in lower proportions: 2.1–7.7% of the AR. Although the degradation products observed in raw and processed commodities are similar, the presence of desmethyl chlorpyrifos-methyl (DEM) is expected to be more important in processed commodities.

Det angives i denne opinion, at der mangler toksikologiske data for metabolitten desmethyl-chlorpyrifos-methyl. Indtil disse foreligger vurderes metabolitten at have samme toksicitet som chlorpyrifos-methyl.

Følgende processing faktorer angives i opinion fra 2017:

(a) Residue definition in processed commodities: sum of chlorpyrifos-methyl and desmethyl chlorpyrifos-methyl, expressed as chlorpyrifos-methyl

Processed commodity	Number of studies ^(a)	Processing factor (PF)	
		Individual values	Median PF
Residue definition in raw agricultural commodities: chlorpyrifos-methyl			
Robust processing factors (sufficiently supported by data)			
Citrus, peeled ^(b)	14	<u>Oranges:</u> 0.01; 0.01; 0.04; 0.04; 0.05; 0.05; 0.05; 0.05; 0.06; 0.07; 0.08; 0.08 <u>Mandarins:</u> 0.03; 0.05	0.05
Citrus, juice	4 ^(c)	0.01; 0.02; 0.04; 0.08	0.03
Apples, juice (extrapolated to pears)	4 ^(c)	0.03; 0.06; 0.14; 0.50	0.10
Apples, sauce	4 ^(c)	0.03; 0.06; 0.14; 0.50	0.10
Table grapes, dried (raisins)	6	0.52; 0.58; 1.7; 2.7; 2.8; 5.9	2.2
Wine grapes, juice	6	0.06; 0.07; 0.09; 0.40; 0.40; 0.77	0.24
Wine grapes, wet pomace	6	0.67; 2.0; 3.3; 3.3; 12.2; 12.8	3.3
Wine grapes, red wine (unheated)	6	0.05; 0.08; 0.18; 0.19; 0.32; 0.72	0.18
Tomatoes, juice	4 ^(c)	0.02; 0.02; 0.05; 0.06	0.03
Indicative processing factors (limited data set)			
Oranges, marmalade	2	0.04; 0.09	0.07
Apples, dry pomace (extrapolated to pears)	2	4.3; 19.9	12
Apples, wet pomace (extrapolated to pears)	2	1.5; 5.6	3.5
Pears, canned	2	0.07; 0.13	0.10
Tomatoes, peeled and canned	2	0.03; 0.04	0.04
Tomatoes, unpeeled and canned	1 ^(d)	0.29	0.29
Tomatoes, sauce	2	0.43; 0.73	0.58
Tomatoes, paste	2	0.89; 0.91	0.90
Tomatoes, ketchup	2	0.38; 0.48	0.43
Tomatoes, dried	2	4.0; 5.4	4.7
Wine grapes, dry pomace	1 ^(d)	33	33
Wine grapes, must	1 ^(d)	1.0	1.0
Residue definition in raw agricultural commodities: sum of chlorpyrifos-methyl and desmethyl chlorpyrifos-methyl, expressed as chlorpyrifos-methyl			
Indicative processing factors (limited data set)			
Barley, brewing malt	2	0.14; 0.14	0.14
Barley, beer	2	0.01; 0.01	0.01
Wheat, whole-meal flour (extrapolated to rye)	2	1.1; 1.2	1.2

Wheat, whole-meal bread (extrapolated to rye)	2	0.56; 0.79	0.67
Wheat, white flour (extrapolated to rye)	2	0.22; 0.24	0.23
Wheat, white bread (extrapolated to rye)	2	0.14; 0.14	0.14
Wheat, bran (extrapolated to rye)	2	2.9; 3.1	3.0

- (a): Studies with residues in the RAC at or close to the LOQ were disregarded.
- (b): The residue definition for processed commodities does not apply to peeled fruits as these processed commodities are not subject to hydrolysis. Therefore, the calculated PF refer to chlorpyrifos-methyl residue levels in both raw and processed commodities.
- (c): Two studies performed with analysis of desmethyl chlorpyrifos-methyl showed that this compound remained below the LOQ in these processed items. Therefore, the PF were derived considering only the residue levels of the parent compound in raw and processed commodities. It also allows using results from two other studies where only analysis of the parent compound was performed.
- (d): Analysis for the metabolite desmethyl chlorpyrifos-methyl was not carried out in the available studies and these PF are therefore considered indicative. However, overestimated processing factors can be derived considering the levels of total 3,5,6-TCP (which includes chlorpyrifos-methyl and desmethyl chlorpyrifos-methyl in addition to 3,5,6-TCP) in processed commodity and the levels of chlorpyrifos-methyl in raw agricultural commodities.

(b) Optional residue definition (raw and processed commodities): sum of 3,5,6- TCP and its conjugates, expressed as 3,5,6-TCP

Processed commodity	Number of studies ^(a)	Processing factor (PF)	
		Individual values	Median PF
Robust processing factors (sufficiently supported by data)			
Citrus, peeled	14	<u>Oranges:</u> 0.01; 0.03; 0.08; 0.09; 0.11; 0.12; 0.12; 0.12; 0.12; 0.14; 0.14; 0.14 <u>Mandarins:</u> 0.05; 0.11	0.12
Citrus, juice	4	0.05; 0.06; 0.12; 0.14	0.09
Table grapes, dried (raisins)	6	0.49; 2.0; 3.6; 3.9; 4.7; 7.9	3.8
Wine grapes, red wine (unheated)	7	0.12; 0.19; 0.19; 0.67; 0.75; 1.2; 1.8	0.67
Wine grapes, juice	4	0.41; 0.69; 0.91; 2.9	0.8
Wine grapes, wet pomace	4	1.3; 4.5; 5.1; 6.6	4.8
Wheat, whole-meal flour (extrapolated to rye)	3	0.35; 0.51; 0.79	0.51
Wheat, whole-meal bread (extrapolated to rye)	3	0.08; 0.61; 0.76	0.61
Wheat, white flour (extrapolated to rye)	3	0.01; 0.06; 0.08	0.06
Wheat, white bread (extrapolated to rye)	3	0.12; 0.13; 0.26	0.13
Wheat, bran (extrapolated to rye)	3	0.91; 2.3; 7.2	2.3
Indicative processing factors (limited data set)			
Oranges, marmalade	2	0.05; 0.11	0.08
Apples, juice (extrapolated to pears)	2	0.11; 0.59	0.35

Apples, dry pomace (extrapolated to pears)	2	0.8; 21	10.8
Apples, wet pomace (extrapolated to pears)	1	0.08	0.08
<hr/>			
Apples, sauce	2	0.39; 0.59	0.49
Pears, canned	1	0.08	0.08
Wine grapes, dry pomace	3 ^(b)	3.4; 7.3; 8.4	7.3
Wine grapes, must	3 ^(b)	0.19; 0.33; 1.5	0.33
Wine grapes, red wine (heated)	1	0.75	0.75
Tomatoes, sauce	2	1.5; 1.7	1.6
Tomatoes, juice	2	0.66; 0.86	0.76
Tomatoes, unpeeled and canned	1 ^(b)	0.66	0.66
Tomatoes, peeled and canned	1	0.51	0.51
Tomatoes, paste	1	8.3	8.3
Tomatoes, ketchup	1	0.88	0.88
Rape seed, crude oil	1	0.48	0.48
Rape seed, refined oil	1	0.62	0.62
Rape seed, meal/press cake	1	0.86	0.86
Cotton seed, crude oil	1	1.2	1.2
Cotton seed, refined oil	1	1	1
Cotton seed, meal/press cake	1	0.80	0.80
Barley, brewing malt	2	1.2; 2.7	2.0
Barley, beer	2	0.15; 0.28	0.2
Maize, flour	1	0.08	0.08
Maize, crude oil	1	0.08	0.08

(a): Studies with residues in the RAC at or close to the LOQ were disregarded.

(b): Since analysis for desmethyl chlorpyrifos-methyl was not carried out, it was not possible to recalculate the absolute levels for 3,5,6-TCP and its conjugates by subtracting the contribution of the parent compound and desmethyl chlorpyrifos-methyl to the total residue hydrolysed as 3,5,6-TCP. Consequently, this processing factor may be overestimated and is therefore considered tentative.

Litteratur

EFSA 2012: Modification of the existing MRLs for chlorpyrifos in various crops and in products of animal origin

EFSA 2014: Conclusion on the peer review of the pesticide human health risk assessment of the active substance chlorpyrifos

EFSA 2011: Modification of the existing MRLs for chlorpyrifos-methyl in various crops
European Food Safety Authority

EFSA 2017: Review of the existing maximum residue levels for chlorpyrifos-methyl according to Article 12 of Regulation (EC) No 396/2005