Cross-contamination of oilseeds by insecticide residues during storage

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Abstract

Pesticide residues are found in oilseeds (rapeseed and sunflower) and crude oils: they are mainly organophosphate insecticides (pirimiophos-methyl, malathion when authorized) used in empty storage facilities and for direct application to stored cereal grain. Even if some secondary pests are found in stored oilseeds, French regulations do not allow use of these insecticides on stored oilseeds. These residues arise from cross-contamination from storage bins and grain handling equipment of grain stores, and not from illegal use. This uptake of insecticide residues from their storage environment by oilseeds may lead to residue contents that exceed regulatory limits. A three-year investigation in grain storage companies allowed us to follow the course of sunflower batches and rapeseed batches during storage seasons 2006-2007, 2007-2008 and 2008-2009, from reception at the storage facility to outloading. Each of these batches was sampled at outloading, and was analyzed for insecticide residues. Traceability of oilseeds established by grain-store managers allowed us to identify cross-contamination sources. The insecticides that were most commonly detected were pirimiophos-methyl, malathion, and dichlorvos (in sunflower 2006-2007), plus chlorpyriphos-methyl and deltamethrin. Pirimiophos-methyl was the most commonly detected active substance, and caused the most cases of non-accordance with regulatory levels in rapeseed. Cross-contamination could have occurred when cereal grains were treated upon receipt, when rapeseed was also delivered, especially when treatments were done systematically to the cereal grains. For sunflower, the main cross-contamination hazard resulted from treatment of cereals at the period of receipt or at their outloading, just before sunflower seeds batches were outloaded. Another situation led to cross-contamination, but generally at a lower extent: oilseeds stored in bins that contained previously treated cereals, or loaded in empty bins with handling equipment treated before the receipt of oilseeds.

Keywords: Oilseed storage, Cross-contamination, Insecticide residues, Rapeseed, Sunflower

1. Introduction

Post-harvest insecticide residues can be sometimes found at low levels, however, on oilseeds stored in France no insecticides can be applied directly during storage, even if some secondary insect pests are found in the stored oilseeds (Dauguet et al., 2005). Consequently, maximum residue levels (MRLs) allowed by European regulations are very low (mostly at the lower limit of analytical determination): 0.05 $mg.kg^{-1}$ for pirimiophos-methyl, 0.05 $mg.kg^{-1}$ for chlorpyriphos-methyl on rapeseed and sunflower; 0.1 $mg.kg^{-1}$ for deltamethrin in rapeseed and 0.05 $mg.kg^{-1}$for deltamethrin in sunflower. No MRL existed for malathion during this study, so it should not be found beyond the analytical limit of quantification (10 $\mu g.kg^{-1}$); but since September 2008 the MRL for malathion in oilseeds is 0.02 $mg.kg^{-1}$ (European Communities Commission (ECC) regulation n° 839/2008 of 31 July 2008).

These insecticide treatments are authorized on stored cereals and corn as grain protectants, and on empty storage and handling equipment as control agents for residual insect populations in empty granaries. Pirimiophos-methyl and malathion were the most common insecticides used during this study, except for the 2008-2009 storage season for when malathion was used. Dichlorvos and malathion, banned by the EU in May 2008, could be used only until 1 December 2008. As the MRL for dichlorvos was revised to be less than 0.01 $mg.kg^{-1}$ in cereals beginning in November 2006, this could no longer be used. The MRL of malathion was not lowered in cereals before withdrawal late in 2008, but it could be still be used until 2007-2008.

We hypothesized that a cross-contamination could result when various kinds of seeds, cereals and oilseeds, share the same grain handling equipment and storage systems. This cross-contamination occurred in Canada on rapeseed (Watters and Nowicki, 1982; White et al., 1983; White and Nowicki, 1985), when empty bins were treated with organophosphate insecticides (bromophos, malathion, fenitrothion). Canadian grain store managers were warned that treating cereal grain before storing rapeseed through the same handling equipment could lead to residues above the maximum allowable limits.

Uptake of pirimiophos-methyl by a single-layer of rapeseed or wheat on galvanized-steel surfaces was demonstrated in a laboratory study (Dauguet et al., 2007). It was shown that, for small bins (less than 50 tons), it could lead to residue contents above regulatory limits. In order to improve our knowledge about this post-harvest insecticide residues cross-contamination, especially in large elevators, an investigation was carried out with the collaboration of several French grain storage companies on sunflower seeds during the 2006-2007 storage season (Dauguet, 2007). second study was done on rapeseed from the 2007 harvest (Dauguet, 2009). Dichlorvos was not used during the storage season 2007-2008, because grain protection strategies changed in France. Rapeseed is harvested in June-July, about at the same period for cereal harvest (winter wheat and barley). A third study on rapeseed and sunflower was carried out during the 2008-2009 storage season.

2. Materials and methods

The process adopted for these three surveys on oilseeds was as follows.

First, we asked storage managers to trace oilseed lots from each step from delivery and receipt to outloading.

Second, we sampled each batch representative of oilseed delivered at the storage facilities ("first sample") and ensured safe storage of these samples. These samples were kept for long-term storage if we suspected that contamination by pesticide residues occurred before receipt at the surveyed grain store.

Third, we obtained a representative mean sample of outloaded oilseed, in order to constitute a "final sample", when the traced lot was downloaded for sale (storage time variable from one to 8 mo after harvesting). The residue content was determined in all these "final samples". The sampling method was done according to the standard for moving seeds, for contaminant quantification, with heterogeneous distribution determination, PR EN ISO 24333: 2006. For each grain bin, twenty five samples were done for each 500-Metric-tonnes-batch evenly distributed during the outloading of the grain bin (one sample each 20 t).

Fourth, we asked managers to fill out a questionnaire called "traceability" which recorded each step from receipt to outloading.

Determination of insecticide residues content in all "final samples" was done by an analytical laboratory ITERG (Pessac, 33, France) for samples taken during 2007 and 2008. In brief, the residue content in seeds was determined through the following protocol: 1) Soxhlet extraction of oil with hexane (NF EN ISO 659); 2/ pre-purification with acetonitril and freezing, purification with solid phase extraction C18 and Florisil cartridges; and 3/ analysis by gas chromatography with NPD detection (organophosphates) or ECD detection (pyrethroid). For 2009, the laboratory of CETIOM in Ardon (France) determined the residues using: 1/ a solid-liquid extraction with isooctane and liquid-liquid extraction with acetonitrile; 2/ purification with SPE C18 and Florisil cartridges for organochlorines and pyrethroids, and 3/ analysis by GC-NPD (organophosphorus) or GC-ECD (organochlorines and pyrethroids).

3. Results

3.1. Residues content in oilseeds and MRL

Twenty-eight samples of sunflower seeds in 2007, twenty-two samples of rapeseed in 2008, and thirty samples of sunflower and thirty-two samples of rapeseed in 2009 were analyzed (Table 1-4).The range of insecticide active substances that are used on cereals or for storage facilities treatment that were detected on rapeseed were pirimiophos-methyl, malathion, chlorpyriphos-methyl and deltamethrin. The most frequently detected substance was pirimiophos-methyl, which was detected in amounts over the lower limit in 55% of samples in 2008 and 37.5% in 2009. This substance also caused the most cases of non-compliance with the MRLs, (32 % of the samples in 2008 and 9.4% in 2009). The concentrations of pirimiophos-methyl measured in rapeseed samples decreased in samples taken in 2008 compared to 2009. Pirimiophos-methyl was also the most commonly detected substance in sunflower seeds (more than the quantification lower limit in 39% of samples in 2007, and in 20% of samples in 2009). The mean concentration of pirimiophos-methyl in sunflower seeds was similar in 2007 and 2009, 19 µg/Kg^{-1} in 2007 and 25 µg/ Kg^{-1} , respectively.

Dichlorvos was detected in the samples from 2007-2008 because of the new regulations. Similarly, malathion was detected in amounts in excess of the MRL in samples 2007 and 2008 (18% of samples of sunflower seeds in 2007, and 18% of samples of rapeseed in 2008) but not in the samples from 2008-2009.

Table 1 Analytical results (expressed in µg kg^{-1}) on the 28 final samples of sunflower seeds (storage campaign 2006-2007).

	LQ	MRL	Mean	Median	Standard deviation	9th decile	Maxi	% samples ≥ LQ	% samples > MRL
Pirimiphos-methyl	10	50	19	5	55	29	295	39%	4%
Malathion	10	-	8	0	25	17	125	18%	18%
Chlorpyriphos-methyl	10	50	0	0	-	-	10	4%	0%
Deltamethrin	10	50	-	-	-	-	Und.	0%	0%
Dichlorvos	10	10	21	0	79	27	422	29%	21%

LQ: limit of quantification, MRL: maximum residues limit; Und.: undetected

Table 2 Aanalytical results (expressed in µg kg^{-1}) on the 22 final samples of rapeseed (storage campaign 2007-2008).

	LQ	MRL	Mean	Median	Standard deviation	9th decile	Maxi	% samples ≥ LQ	% samples > MRL
Pirimiphos-methyl	10	50	130	22	266	335	1117	55%	32%
Malathion	10	-	19	0	69	16	322	18%	18%
Chlorpyriphos-methyl	10	50	3	0	9	0	31	9%	0%
Deltamethrin	10	100	1	0	3	0	13	5%	0%
Dichlorvos	10	10	-	-	-	-	Und.	0%	0%

LQ: limit of quantification; MRL: maximum residues limits; Und.: undetected

Table 3 Analytical results (expressed in µg kg^{-1}) on the 32 final samples of rapeseed (storage campaign 2008-2009).

	LQ	LMR	Mean	Median	Standard deviation	9th decile	Max	% ≥ LQ	% > MRL
Pirimiphos-methyl	10	50	16	0	5	31	212	37,5%	9.4%
Malathion	10	20	0	0	2	0	13	3,1%	0%
Chlorpyriphos-methyl	10	50	1	0	40	0	24	6,3%	0%
Deltamethrin	10	100	3	0	2	5	64	6,3%	0%
Dichlorvos	10	10	-	-	-	-	Und.	0%	0%

LQ: limit of quantification, MRL: maximum residues limits; Und.: undetected

Table 4 Analytical results (expressed in µg kg^{-1}) on the 30 final samples of sunflower seeds (storage campaign 2008-2009).

	LQ	LMR	Mean	Median	Standard deviation	9th decile	Max	%>LQ	%>LMR
Pirimiphos-methyl	10	50	25	0	106	13	578	20%	6.7%
Malathion	10	20	-	-	-	-	Und.	0%	0%
Chlorpyriphos methyl	10	50	-	-	-	-	Und.	0%	0%
Deltamethrin	10	50	1	0	3	5	14	3,3%	0%
Dichlorvos	10	10	-	-	-	-	Und.	0%	0%

LQ: limit of quantification, MRL: maximum residues limits; Und.: undetected

3.2. Traceability of cross-contamination situations

Five cases leading to cross-contamination were identified:

1) K1, treatment of cereals at outloading, just before outloading oilseeds;
2) K2 outloading of cereals, treated at their receipt, just before outloading of oilseeds,
3) K3 storage of treated cereals in the same bin just before storage of oilseeds;
4) K4 treatment of empty bin and of handling equipment before receiving oilseeds;
5) K5 receipt of oilseeds at the same time that cereals treated at receipt (it concerned only rapeseed).

When no cross-contamination occurred it was classified as K0.

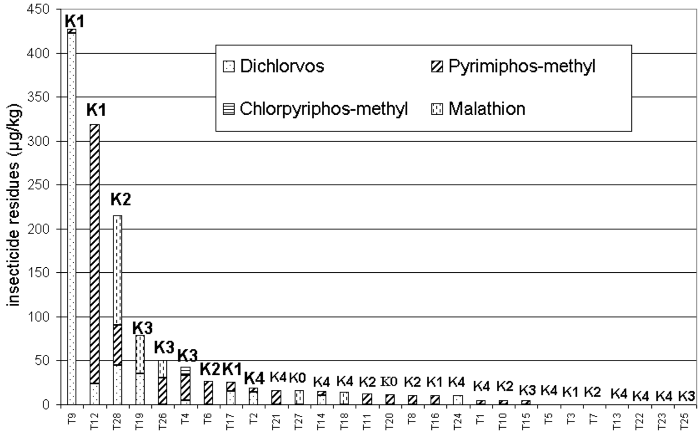

Figure 1 Distribution of the five cases of pesticide residues cross-contamination for each sunflower seeds batch (2006-2007).

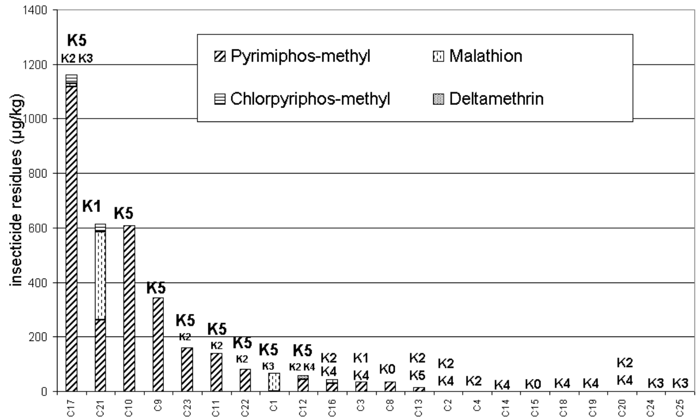

Figure 2 Distribution of the five cases of pesticide residues cross-contamination for each rapeseed batch (2007-2008).

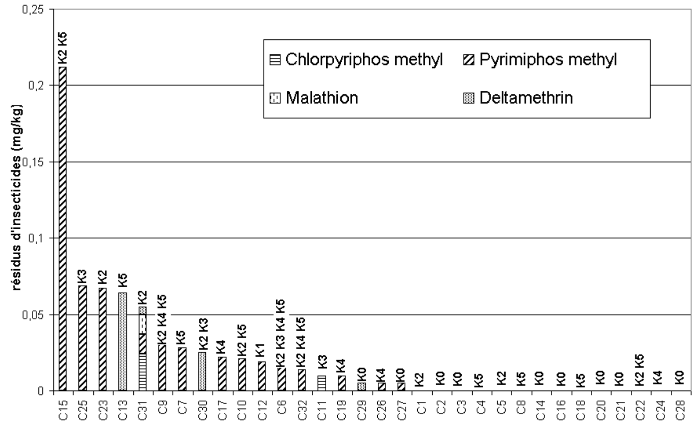

Figure 3 Distribution of the five cases of pesticide residues cross-contamination for each rapeseed batch (2008-2009).

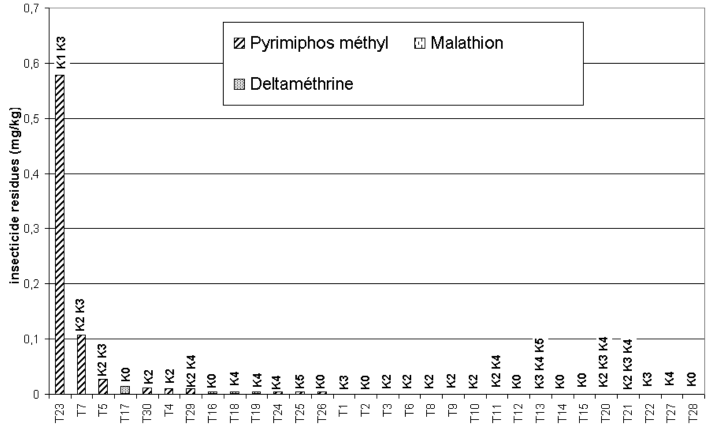

Figure 4 Distribution of the five cases of pesticide residues cross-contamination for each sunflower seeds batch (2008-2009).

4. Discussion

It appears that the highest cross-contamination on rapeseed occurred with situation K5 (Figs. 2 and 3). This one is characteristic of rapeseed, which is harvested at the same seasonal period than cereals (wheat, barley) during June-July. Most samples with pirimiophos-methyl above the MRL were from K5 (Fig. 2). Looking at each sample, we can observe that the highest contaminations occurred when treatments on cereals at receipt were systematically carried out. The occurrence of situations with a treatment of cereal batches immediately at their delivery increased in 2007-2008 because dichlorvos was already banned. Before this ban, dichlorvos treatment was more often used when a pest infestation was detected just before commercialization. Today, storage operators seem to prefer a preventive control of pests at the delivery before loading storage bins. In the 2007-2008 survey, it was observed that 81% of cereal deliveries were systematically or occasionally treated at their receipt. In the 2008-2009 investigation (on rapeseed and sunflower), it was observed that 75% of the delivered cereal grain batches were systematically or occasionally treated at their receipt at the silo. It was also shown that treatment of cereals at receipt could also lead to the cross-contamination situation K2 and K3, which were also frequent on rapeseed in 2008-2009 survey (Fig. 3).

The situation K5 can also be linked to a problem with insecticide application equipment: unsatisfactory proof for insecticide aerosol droplets release from insecticide treatment system, cereal treatment not stopped after the emptying of the handling circuit (leading to a direct accumulation of residues on empty handling equipment), possible delay for switching off a cereal treatment before loading the handling system with a rapeseed batch received just after several cereal batches. These situations could neither be checked nor validated in our investigation.

The situation K1 was less frequent than the situation K5, but can also lead to cross-contaminations. It was this situation, as in the previous investigation on sunflower, that led to the highest contaminations when treatment of cereals was systematic at outloading (Fig. 1). It can also occur on rapeseed. In the case C21 (Fig. 2), malathion and chlorpyriphos-methyl were not used during the storage season 2007-2008, but was used during previous seasons. This silo was made of concrete; so we hypothesized this surface can retain residues more than a year. The situation K4 did cause few problems, except if it was associated to other risky situations. On sunflower (Figs.1 and 4), the highest contaminations were observed when treatment was systematic at outloading (K1) in 2006-2007. Even though dichlorvos had been banned, other practices led to classification of sunflower seeds as K2 and K3. This was most likely caused when silos treated the cereals upon receipt. Our study in real situations showed that cross-contaminations of oilseeds by post-harvest insecticide residues exist, and can sometimes lead to residue contents above regulatory tolerances. The highest risk of contamination for rapeseed appears to occur when cereals are systematically treated at receipt, at the same time that rapeseed is received, using the same conveyor circuits. Other identified cases can also lead to slighter contamination. We identified several situations within a storage facility that can increase the risk level for the cross-contamination. We did not identify all possible sources of residue contamination, but one more possibility for contamination is leakage of insecticide by the application equipment.

We noticed differences in cross-contaminations between sunflower and rapeseed, difference that we could relate to a very different harvest period for these two oilseeds. And also, we noticed a change between the three years of investigation: the withdrawal of dichlorvos had adverse indirect effects in leading to preventive strategies with more frequent treatments of organophosphates applied for preventative protection against storage insect pests.

To reduce cross-contaminations, we can advise storage managers to avoid sharing same receipt circuits when cereals are systematically treated, and to avoid accumulation of risky situations. It is also very important to periodically verify the proper use of insecticide treatment equipment. This investigation allowed us to make the storage companies aware about this issue, and to help them to understand how cross-contaminations can occur in their silos and how to avoid them, knowing that each silo is different than others.

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