50 g/m³ (700 ppm)	2	435	Top-left	100	100	100	100	100	100
			Top-right	100	100	100	100	100	100
			Middle	100	100	100	100	100	100
			Bottom-left	100	100	100	100	100	100
			Bottom-right	100	100	100	100	100	100
Control (Unfumigated)	3			0[1/]	0	0	0	0	0

[1/] Mean of 3 replications

Tab. 3 Phosphine concentrations inside the stacks during milled rice fumigations with $ECO_2FUME^®$ fumigation at different dosages and exposure times.

Application	Dose	Time	Stack	Volume of	Location	Phosphine concentration (ppm) Hours 1	18	24	42	48	66
5-kg in plastic bag	50 g/m³ (700 ppm)	2	55	2.73	Top	>2000	1,325	1,289	1,213	1,195	
					Middle	>2000	1,293	1,295	1,225	1,197	
					Bottom	>2000	1,284	1,297	1,255	1,199	
			46	2.32	Top	>2000	853	860	829	819	
					Middle	>2000	864	849	837	826	
					Bottom	>2000	867	855	845	830	
					Inside plastic bag	-	805	875	812	811	
		3	50	2.48	Top	>2000	1,365	1,369	1,283	1,144	1,060
					Middle	>2000	1,360	1,361	1,281	1,147	1,065
					Bottom	>2000	1,359	1,380	1,279	1,148	1,069
			50	2.50	Top	>2000	1,145	1,125	1,070	1,069	1,075
					Middle	>2000	1,163	1,112	1,085	1,065	1,078
					Bottom	>2000	1,173	1,120	1,095	1,075	1,085
					Inside plastic bag	-	999	1,001	1,104	1,101	1,127
1,000-kg jumbo bag	35	3	314	11.22	Top	>2000	1,239	1,225	1,230	1,171	910
					Middle	>2000	1,227	1,231	1,242	1,189	926
					Bottom	>2000	1,244	1,237	1,259	1,236	940
	50	2	435	21.77	Top	>2000	1,492	1,494	1,150	986	
					Middle	>2000	1,505	1,510	1,146	1,087	
					Bottom	>2000	1,512	1,514	1,192	1,098	
					Inside jumbo bag	-	1,490	1,534	1,483	1,493	

Residual behaviour of phosphine in different commodities

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Abstract

Phosphine is one of the most common active substances used in storage protection worldwide. As it is very efficient amongst a broad range of living organisms, it has become the favoured product after phasing out methyl bromide in 2010, as it can be used in many commodities.

In 2005, the regulation 396/2005 was enacted and came into force in 2008. With this, the European commission started to evaluate residues arising from the use of a pesticide and to set maximum residue levels (MRLs) for safe and regulated food trade.

To proof residue levels are below MRL and therefore far below concerning concentrations of phosphine in food or feed, residue studies are permanently conducted. In addition to support MRL settings, the intention of these trials is to determine withholding periods needed in storage protection, corresponding to PHI (pre harvest interval) for field and glasshouse treatments.

Results of those studies show different levels and differences in decrease of residues after defined time periods. Thus, withholding periods for various commodities can differ. Residue trials with repeated exposure were conducted as well to determine possible additive effects.

Keywords: Phosphine, maximum residue level (MRL), withholding period

Regulatory background

To ensure safe and fair trading conditions among the EU member states and non-European countries, regulation 396/2005 came into force on 1st of September 2008. The major aim of this regulation was to set maximum residue levels (MRL) for pesticide residues in and on cereals, foodstuff of animal origin, and products of plant origin in one regulation only. This became necessary due to formerly separate regulations, inhibiting harmonization and complicating registration processes during plant protection authorization. Besides, the setting aims to avoid unacceptable risks posed by residues in treated commodities to humans and in animals feeding. MRLs are being reviewed and updated on a regular basis.

To evaluate a potential risk arising from treating goods with plant protection products (but also biocides), manufacturer of active contents and products composing those actives destined for plant protection uses are obliged to characterize the residual behavior of the product inside each targeted commodity. One important basis to set an MRL for a commodity or a group of commodities is provided by residue trials.

Behaviour of phosphine

There are many forms of phosphine (PH_3) emitting products, such as compacts, bags and plates. The reaction is based on the very simple reaction of the metal phosphide with humidity and air.

During fumigation with metal phosphide based formulations, the small molecule phosphine is being formed as a reactive intermediate. As it has many advantageous properties, the possibilities of use are various. One of these is the excellent capability of the gas to penetrate inside the commodity, facilitating all stages of stored product pests to be effectively eliminated.

As the commodities vary highly in nutrient composition, structure, and size, the phosphine molecules show very different binding behaviours and elimination times inside the goods.

It has become clear that these characteristics are essential during evaluating MRLs and play a crucial role in setting withholding periods after fumigation.

Materials and Methods

To represent a possible worst-case scenarios, different storage goods from commodity groups defined as in COMMISSION REGULATION (EU) 2016/1785 (2016) are chosen to be fumigated with different metal phosphide formulations containing magnesium or aluminium phosphide. All trials are conducted following GLP principles set be OECD.

In the present study, 20 kg of different storage goods were placed in 4 different airtight containers. After exposing the test items to 5 g PH_3/m^3 (Degesch Magtoxin) and 5.5 g PH_3/m^3 (Degesch Plate) for 5 days, and to 10 g PH_3/m^3 (Phostoxin Tablet and Detia Gas-Ex-B) for 14 days, samples were taken in intervals to determine residues. The longest withholding period was 28 day after aeration. To ensure negative control levels, residue analysis were conducted prior to fumigation.

The dosage and exposure time represented the highest registered doses and exposure times in the EU.

Commodities tested were:

cereals

tobacco

flour (wheat)

coffee beans

cocao beans

dried fruit (apricot)

dried vegetable (leak)

legumes (lentils)

expeller (oilseed rape press cake)

oilseed (flaxseed)

hay

herbs (dried, marjoram)

malt (dried)

nuts (hazelnut)

pistachios

coriander

medical plants (blossoms, chamomille)

liquorice

spices (leaf, laurel leaves)

black tea

potato starch

The treated commodities were sampled and stored deep frozen until analysis, which was conducted within 24 hours after sampling.

Results

No residues were detected in any of the control samples prior to fumigation.

For all tested commodities, the residue analysis directly after the end of aeration showed values below 0.05 mg/kg, except for hazelnuts and pistachios. For the two products, Degesch Plate and Detia Gas-Ex-B, residues after right aeration were increased in hazelnuts and pistachios. For Degesch Plate treatments, the residues in hazelnuts and pistachios were below 0.05 mg/kg after 14 days, while for Detia Gas-Ex-B, pistachios achieved values below 0.05 mg/kg after 7 days and hazelnuts after 21 days.

Discussion

The trials show a different behavior of storage goods regarding elimination of phosphine. Especially, high fat containing representatives of the group of tree nuts show a slower removal of the gas. Therefore, the withholding periods after aeration are increased.

As analytical methods have become significantly more accurate, residue trials were and are necessary to determine MRLs. Withholding periods are therefore a necessary and important indication for food and feed industry to be regarded on behalf of safe and fair trading or processing of the goods after fumigation.

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