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Mortality of Three Stored Product Pests Exposed to Sulfuryl Fluoride in Laboratory and Field Tests

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Abstract: Effectiveness of sulfuryl fluoride(SF) for the control of three stored pests was investigated as alternatives to methyl bromide(MB) and resistance to phosphine(PH_3). The toxicity test indicated that SF at low concentrations was effective to control *Sitophilus oryzae*(L.), *Rhyzopertha dominica* Fabricius and *Tribolium castaneum*(Herbst). In addition, 5.94g/m^3 SF mixed with 14.27g/m^3 CO_2 were used for fumigation of grain for 30d. The gas mixture was effective in the control of the adult pests and F_1 progeny without negative effects concerning the quality of treated wheat, long – grain non – glutinous rice and medium to short – grain non – glutinous rice.

Key words: Sulfuryl fluoride (SF), *Sitophilus oryzae*, *Rhyzopertha dominica*, *Tribolium castaneum*, gas mixture, CO_2

Introduction

Since about 1950, China has started to fumigate against stored grain pest insects to prevent losses. The fumigants included mainly chloropicrin, methyl bromide and hydrocyanic acid. Phosphine(PH_3) is in use as fumigant in China since about 1960. Methyl bromide(MB) and PH_3 have been developed to bethe main fumigants in the grain storage industry.

For a long time, PH_3 was widely used in grain storage because of special advantages in cost, efficacy, application method, low residual toxicity and worker safety; whereas, after long and exclusive use of PH_3, stored grain insects have increasingly developed resistance to this gas. Therefore, in some places many failures of fumigation occurred after using PH_3 to kill insects. PH_3 fumigation requires improved gas tightness of the fumigated enclosure, temperature higher than 15℃, and longer treatment time. Therefore, many grain stores, especially, those with old structures and lower gas tightness preferred to use methyl bromide fumigation instead. However, with greater awareness of environmental protection, methyl bromide was eliminated because of its ozone depleting property to the atmosphere. According to the International Montreal Protocol and related conventions, developing countries were demanded to accept the phase out of methyl bromide in 2015. The Chinese government decided that the grain storage industry of the whole country must not use methyl bromide from January 1, 2007 onwards. At present, the national stored grain insect prevention fumigation mainly relies on PH_3. Using PH_3 for a long time resulted in stored grain insects with fairly high resistance to PH_3. Therefore, it is necessary to study and develop a new chemical, which is efficient, has low mammalian toxicity, does not lead to pollution and will preferably not cause resistance.

Sulfuryl fluoride (SF) is a toxic gas and has been used since 1960 for controlling various insects in wooden buildings especially against termites. It is a universal insecticide and rodenticide. Its mode of action consists in the release of fluoride ions to restrain the circulation of glycolysis and fatty acids, which deprive the necessary energy for the survival of insects. In July 2005, SF was registered in the United States of America, being used as fumigant for the control of stored grain insects. In the beginning of 2008, it was approved for use as fumigant against stored grain insects in China. The fumigant is targeted for the wide use of grain fumigation in China. This paper reports on results of the experiments in providing additional theoretical and practical knowledge for the wide use

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of this new gas for insect pest control.

Materials and Methods

Test place

Toxicity test: Tests were carried out in the Chengdu Grain Storage Research Institute.

Field test: Storehouse No. 29 at Gaomi Grain Depot, which has horizontal warehouse, with brick structure, door and window air-proofed by sheet. The warehouse has a volume of 5 000 m^3, with 3 280 m^3 storage capacity of grain. The gastightness was tested to hold for 40s the pressure decay from 500Pa to 250Pa, which is the national standard for fumigation. The warehouse is equipped with aeration ducts and it has computerized temperature monitoring systems.

Tested Grain

Tests were carried out on 2 500 tonnes of wheat produced at Shandong province, which was stored for two years, with impurities of 5%, moisture content 11.3%. The temperature of the warehouse was 31.6℃, relative humidity 66%, average temperature of grain was 19.3℃, the lowest grain temperature was 12℃, long-grain nonglutinous rice and medium to short-grain nonglutinous rice produced at Sichun province was placed on the surface of the grain in the warehouse.

Tested Insects

ⅰ) Toxicity test

Two weeks old adults of susceptible and phosphine resistant strains of *Sitophilus oryzae*, *Rhyzopertha dominica and Tribolium castaneum* were used for toxicity tests.

ⅱ) Field test

Tested insects were eggs, larvae, pupae and adults of susceptible and phosphine resistant strains of *Sitophilus oryzae*, *Rhyzopertha dominica* and *Tribolium castaneum*. Every cage contained the four developmental stages of the tested insects. The cages were made of nylon meshwork about 15cm(5cm. There were a total of 54 cages used in these tests. Each cage contained 5 g food and 50 adult insects. Each test was carried out on 9 cages containing susceptible and resistant strains of insects.

Fumigant

The SF concentration in the cylinder was 99.5%, that of CO_2 in the cylinder was 99.5%. The ratio of SF: CO_2 used was 1:2.5, the dose of SF was 5.94 g/m^3 and the dose of CO_2 14.27 g/m^3 was used in the mixture.

Equipment

For field tests, caged insects of 15 cm × 5 cm made of nylon meshwork that enabled penetration of the gas were used. For toxicity tests in the laboratory, phosphine was generated on – site and desiccators equipped with recirculation units were used.

Experimantal Methods

Toxicity Test

Laboratory tests to determine the LC_{50} and $LC_{99.9}$ of SF values exposed for 20h and 48h were carried out for *Sitophilus oryzae*, *Rhyzopertha dominica* and *Tribolium castaneum* using the FAO method [1].

Field Test

The field test was carried together with the Chinese Academy of Inspection and Quarantine, Gaomi Grain Depot of Shandong Province and Longkou City Chemical Plant.

ⅰ) Placement of cages with test insects

There were a total of 54 cages that consisted of 3 insect species, 2 strains, 3 test points in the warehouse, and 3 depths in the grain bulk. The three points selected to place the tested insects were in the middle, northeast corner and southwest corner, and every point was tested at three depths of 0.2m, 2.5m and 3.5m deep below the surface.

ⅱ) Fumigation

The fumigation was carried out with a mixture of SF with CO_2. The ratio SF: CO_2 was 1:2.5, the dose of SF was 5.94 g/m^3 and the dose of CO_2 14.27 g/m^3. At the beginning, the fumigants were supplied and recirculated for 4h with the recirculation unit. Subsequently, each third day the gas was recirculated for 2h. The fumigation lasted 30d.

ⅲ) Quality of grain

Germination and other quality parameters were determined after the fumigation of wheat and paddy.

Results

Toxicity Test

The LC_{50} and $LC_{99.9}$ values of SF to control *Sitophilus oryzae*, *Rhyzopertha dominica*, *Tribolium castaneum* using the FAO method[1] for 20h and 48h are shown in Table 1.

Table 1. Response of adult *Sitophilus oryzae*, *Rhyzopertha dominica*, *Tribolium castaneum* towards exposure to SF (25℃ and R. H. 70%).

Strain		Time (h)	LC_{50} (g/m^3)	$LC_{99.9}$ (g/m^3)	Ct (gh/m^3)	dF(degree of freedom)	CHI SQ(95% confidence index)	Reference values
Sitophilus oryzae	S*	20	1.39	3.48	69.60	8	6.17	15.507
		48	0.73	2.06	98.88	6	10.06	12.592
	R*	20	1.27	4.68	93.60	8	2.53	15.507
		48	0.63	1.23	59.04	2	5.47	5.991
Rhyzopertha dominica	S	20	1.06	1.72	34.40	4	2.66	9.488
		48	0.57	0.89	42.72	3	3.75	7.815
	R	20	1.05	1.57	31.40	3	6.28	7.815
		48	0.56	0.94	45.12	5	3.96	11.070
Tribolium castaneum	S	20	2.04	3.06	61.20	6	9.71	12.592
		48	0.88	1.29	61.92	7	3.25	14.067
	R	20	1.97	3.14	62.80	6	7.17	12.592
		48	0.80	1.05	50.40	5	9.75	11.070

*: S: susceptible strains, R: phosphine resistant strains

Field Test

SF concentration in field fumigation

Gas concentrations were not measured in the field tests because of lack of portable gas analyser. But gas samples were taken to the laboratory and the concentrations were measured using gas chromatograph equipped by electron – capture detector. The gas concentration after 11 days of fumigation was 77.078 mg/m^3, and after 30 days it was 0.0367 mg/m^3. It showed the SF concentration is very low after fumigating 11 days.

Effect of field fumigation on insects

Mortality of insects was tested 30d after fumigation, and the data are shown in Table 2.

Table 2. Response of SF fumigating in field.

Tested insect			Mortality(%) southwest corner	Mortality(%) Middle	Mortality(%) northeast corner
adult	*Sitophilus oryzae*	S	100	100	100
		R	100	100	100
	Rhyzopertha dominica	S	100	100	100
		R	100	100	100
	Tribolium castaneum	S	100	100	100
		R	100	100	100
Count the number of adults hatched after 42d					
Eggs, larvae, pupae	*Sitophilus oryzae*	S	0	0	0
		R	0	0	0
	Rhyzopertha dominica	S	0	0	0
		R	0	0	0
	Tribolium castaneum	S	0	0	0
		R	0	0	0

*: S: susceptible strains, R: phosphine resistant strains.

Table 3. Influence of SF on the germinating capacity of the treated grain

grain		germinating capacity(%)			Average germination capacity(%)
		Replicate 1	Replicate 2	Replicate 3	
wheat	Prior to fumigation	96	96	94	95.7
	After fumigation	96	92	96	95
long – grain nonglutinous rice	Before fumigating	86	86	88	86.6
	After fumigating	86	86	86	86
medium to short-grain nonglutinous rice	Before fumigating	94	96	94	95
	After fumigating	94	94	96	95

Table 4. Influence of SF fumigation on quality of paddy

Item	medium to short-grain nonglutinous rice		long-grain nonglutinous rice	
	Prior to fumigation	After fumigation	Prior to fumigation	After fumigation
Brown rice yield(%)	86.1	85.3	78.8	78.7
Crude protein(% dry weight basis)	9.6	9.7	10.0	9.8
Paddy fatty acid value(KOH/dry basis)/(mg/100g)	20.3	19.0	17.7	19.0
Sensory evaluation(%)	87	87	86	85
Yellow-colored rice(%)	0	0	0	0
Colour and luster, odor	normal	normal	normal	normal

Table 5. Influence of SF fumigation on wheat quality

Item	Before fumigating	After fumigating
Gluten water absorption(%)	215	216
Crude protein(% dry basis)	15.0	13.7
sensory evaluation of steamed bread(cent/100)	84.0	82
sensory evaluation of bread(cent/100)	79	77
Viscosity(mm^2/S)	5.6	6.7

Discussion

The test indicated that the mixture of SF ($5.94g/m^3$) and CO_2 ($4.27g/m^3$) to fumigate for 30 d was effective to control insects pest in grain. The fumigation did not deteriorate the quality of treated wheat and paddy.

Compared with methyl bromide, SF has some advantages, such as its physical and chemical properties. The gas does not cause any damage to the ozone layer with better dispersion and infiltration through the fumigated products than methyl bromide. The American DOW Company used *Tribolium confusum* imagoes and large larvae of the black larder beetle to test the insecticidal effect of SF and MB[2]. The results showed that the dosage of SF was less than that of MB under the same conditions. Other research showed that mixed SF and MB had a better effect to control pupae and eggs of the khapra beetle[3]. As for the toxicity on higher animals, SF has not teratogenic, carcinogenic, mutagenic effects[3,4,5].

Additional research using SF on wheat and paddy did not show deleterious influence on their germination rate or their quality, and it could cause complete mortality of adults, larvae and eggs of the tested insects.

Therefore, SF after the phase out of MB, seems to be a suitable fumigant for the grain storage industry,. The implementation of SF would not only provide a new technology for grain storage, but also consolidate the achieved success after removal of MB from the market and prevent the grain storage industry use of MB again.

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