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EVALUATION OF PROFUME® GAS FUMIGANT (SULFURYL FLUORIDE) IN AMBIENT AIR ADJACENT TO A BULK GRAIN STORAGE IN AUSTRALIA

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ABSTRACT

ProFume® gas fumigant (99.8% sulfuryl fluoride, Dow AgroSciences, Indianapolis, IN, USA) has been used for control of mixed age populations of insects infesting grain storages in Australia since 2007. The increased use and reliance on ProFume as a pest management tool in Australia is due in part to the widespread distribution of multiple insect species resistant to commonly used insecticides in grain protection. In particular, high levels of phosphine resistance have been documented in *Cryptolestes ferrugineus* in north eastern Australia, where existing phosphine label rates are no longer effective. In addition to large scale grain storages, fumigations using ProFume have been conducted in a variety of structures including houses, mills, shipping containers, buildings, ships, bag stacks, silo bags, and silos sheds. In Australia, ProFume is championed and distributed by SA Rural Agencies, now a division of A-Gas. SA Rural is also responsible for product stewardship which includes product specific training of fumigators and oversight of compliance in use of ProFume. The safe use of ProFume is of primary concern. One trial was carried out in Australia to monitor ProFume in ambient air around a large scale grain storage during fumigation and aeration. The results demonstrated that the 3 m exclusion zone, currently used for phosphine fumigations, and label directions for ProFume prevent bystander and worker exposure to SF concentrations which exceed permissible levels during fumigation and aeration.

Key words: ozone depletor, stored product fumigant, ProFume gas fumigant, sulfuryl fluoride, product stewardship.

INTRODUCTION

The listing of methyl bromide as an ozone depletor by the Montreal Protocol initiated development work by Dow AgroSciences to find an alternative stored product fumigant. ProFume® gas fumigant (99.8% sulfuryl fluoride [SF], Dow AgroSciences, Indianapolis, IN USA) has been used for control of a range of insects in a variety of structures including houses, mills, shipping containers, buildings, ships, bag stacks, silo bags, silos sheds, and grain bunkers. ProFume has been used for control of mixed age populations of insects infesting grain storages in Australia since 2007 and is registered for control of a variety of insect species in dried commodities. The most common species encountered in grain storages in Australia are: the rusty grain borer *Cryptolestes ferrugineus* (Stephens), lesser grain borer *Rhyzopertha dominica* (F.), flour beetles, *Tribolium spp.*, and rice weevil, *Sitophilus oryzae* (L.), which are all controlled by ProFume. The widespread discovery of insects resistant to phosphine, especially *C. ferrugineus* in north eastern Australia where existing phosphine label rates are no longer effective (Emery *et al.,* 2011), has led to the increased use and reliance on ProFume as a pest management tool (Nayak *et al*., 2010).

In Australia, ProFume is championed and distributed by SA Rural Agencies, now a Division of A-Gas (Australia). SA Rural is a leading supplier of a comprehensive range of fumigation products and services to established agents and distributors throughout Australia and countries in the Asia Pacific region. In conjunction with Dow AgroSciences, SA Rural Agencies introduced Telone®, chloropicrin and ProFume as viable replacements for methyl bromide in Australia.

The use of ProFume brings many benefits to the user, including a product stewardship program and the Fumiguide® Program, a highly effective tool for calculating the dose needed based on pest species, temperature, estimated gas retention and duration of fumigation. Other benefits of ProFume include: a different mode of action for use as a fumigant alternative in phosphine resistance management programs, superior material compatibility (inert to most materials), ease of application and to "top up" a fumigation, and rapid aeration of fumigated commodities.

The safe use of ProFume is of primary concern. The currently available, battery-operated low-concentration SF detectors are too large to use as a clip-on personal monitoring device (such as those available to detect phosphine). This trial was conducted to determine if the standard 3 m exclusion zone established around grain bunkers as a label requirement for ProFume (as it is for phosphine) prevents bystander and worker exposure to SF concentrations above permissible levels.

MATERIALS AND METHODS

The trial was carried out at a grain storage facility operated by GrainFlow in Jondaryan, Queensland, Australia. One metal-sided bunker for sorghum storage was evaluated. The tarped bunker measured approximately 8 m (height) x 34 m (width) x 253 m (length), and stored about 33,500 tonnes of sorghum.

During the fumigant introduction and exposure periods, eight air monitoring stations were positioned 3 m from the basal perimeter of the bunker at the four corners and at two locations midway on each lateral side. Each monitoring location consisted of a stand made of 2.5 cm diameter PVC pipe attached to a commercially available bollard in order to collect an air sample drawn from 1.5 m in height from the ground using a battery-powered (2 size "D" cells) aquarium air pump (Marina, Rolf C. Hagen Corp., Mansfield, MA) modified to have the fresh air intake port connected to 0.64 cm OD Tygon tubing. A Kinar^{TM} 20-L air sample bag, fitted with an on-off valve using 0.64 cm OD Tygon tubing was attached to the pump exhaust port. Air flow rate from the air pump was controlled by a plastic air control valve (Elite) between the pump and quick release connector. The air flow valve was adjusted in ml/min using the small hand screw valve and a mass air flow meter (Cole-Palmer Instruments Co., Chicago, IL,) to provide sufficient sample air without over-inflating the bags according to the planned sampling interval. Air flow rates were 20-30 mL/min for day time sampling and 15 mL/min for overnight sampling. Batteries on the pumps were changed after two days of operation.

At the start and conclusion of each monitoring period, the air flow rate was measured and the time recorded. SF concentrations were measured in the air sample bags using the SF-ExplorIR (Spectros Instruments, Hopedale, MA) which uses non-dispersive infrared sensor technology to measure low SF concentrations. During the daytime, air bags were sampled at two intervals, ~4 h each, during the first four days after fumigant introduction and one interval, ~8 h, at five days after introduction through aeration. Overnight, air bags were sampled at one, ~16 h interval. Prior to initiation of aeration, seven additional ambient air monitoring stations were placed on the east side of the bunker where fumigant was to be vented. Stations were spaced at 20 and 40 m intervals in front of, in back of, and at a 90 degree angle from the exhaust vent of the aeration fan. During aeration, air bags were sampled at ~8 h during the first day of aeration and after ~15.5 h overnight.

The SF concentration was measured ca. 1 m in the grain at 16 locations; nine along the bunker peak and seven along the lower perimeter, about 3 m from the metal wall, at each corner and intermediate on the western and eastern sides. Fumigant monitoring hose (0.32 cm OD x 90 m long) was folded at the terminal end and taped with electrical tape, and at least ten 1-mm diameter holes were punched into the hose before the fold using a leather tool punch. This was done to prevent grain from lodging inside the hose during insertion and monitoring. The monitoring hose was inserted using a grain sample probe through a tarp slit, which was sealed with double-sided, 1 mm thick butyl tape. The labeled, proximal ends of the monitoring hoses extending outside the grain bunker were connected to a manifold (LeBeau Inspections, Inc., Mt. Sterling, OH). An electric pump powered by a car battery was used to rapidly draw air samples from within the grain mass to the manifold. SF concentrations in the air samples were measured using an SF-ContainIR version 1.88 (Spectros Instruments, Hopedale, MA) consisting of a portable, battery-operated monitoring device which also uses non-dispersive infrared (NDIR) sensor technology to measure SF. SF concentrations were measured at least twice daily throughout the fumigation exposure period.

The target dose, calculated using the Fumiguide Program, was 24 g m^{-3} of ProFume. A total 1021 kg of ProFume (18 cylinders of ProFume) was calculated based on the tonnage of grain stored and was applied using commercial methods. ProFume was introduced into the bunker through 0.44 cm ID introduction hose that was approximately 150 m in length. A manifold was used at the terminal end to connect two short lengths of 0.44 cm ID introduction hose which were inserted through slits cut in the tarp about 3 m down from the peak on the east and west sides of the bunker. These insertions occurred at ~15 m intervals along the peak. Introduction was on the 22 September, 2011. Each slit in the tarpaulin was sealed with butyl tape after the introduction hose was removed. Additional gas 56.7 kg was introduced on 27 September 2011 in order to achieve the specified dose in this area of the bunker. The introduction hose configuration was the same as described previously, with two hose insertions made on the northeast corner of the bunker. This was the only section of the bunker in which monitoring indicated the accumulated dosage was less than required for control of target pests. The amount of ProFume added was calculated to obtain the required accumulated dosage based on the measured conditions of confinement and the remaining fumigation exposure period. All fumigant introductions were conducted by certified applicators of ProFumigation, Inc.

The fumigant exposure period was 11 days due to scheduling of aeration to begin on Monday, 3 October 2011 when the required grain facility personnel were present. Fumigant aeration was carried out using a custom built ventilation unit, consisting of an Aerovent fan powered by a 37.8 amp electric motor (Western Electric) mounted on a trailer installed on the southeast corner of the bunker. The tarp in the northwest corner of the bunker was unsealed to permit fresh air input. The aeration fan was started to initiate aeration at 9:56 am, 3 October 2011 and operated continuously throughout aeration which was completed at 9:40 am the next day. Readings were taken using an SF-ExplorIR until the bunker was certified cleared. Then all sampling equipment (hoses, temperature data loggers, and bioassays) in the bunker were removed.

RESULTS AND DISCUSSION

The SF accumulated dosage in the grain was sufficient for the targeted insect control. The lowest accumulated dosages of 848 and 880 g h m^{-3} were at the north end of the bunker where additional ProFume was added.

SF was detected in four air sample bags, representing three sample locations and two sample intervals; introduction and initial fumigation exposure period. For all other sample locations and intervals, including aeration, no SF was detected in the air sample bags. The highest SF concentration measured in an air bag was 3 ppm, which is the permissible exposure limit of ProFume for workers and bystanders. The 24 hour Time Weighted Averages (TWAs) of SF for introduction and initial fumigant exposure for the three locations in which fumigant was detected were 0.17 ppm for two locations and 1.15 ppm for one location. These TWAs are well below the 3 ppm TWA for SF established in Australia for protection of workers and bystanders. TWAs could not be calculated for other monitoring locations and time periods because concentrations of SF were below the limit of detection (1 ppm) of the SF-ExplorIR. Therefore, any potential exposure of workers and bystanders to SF at the 3 m exclusion zone boundary during the fumigation and aeration period periods would have been well below the TWA of 3 ppm for a 24 hour exposure.

These results demonstrate that at the 3 m exclusion zone worker and bystander exposure to ProFume was well below the permissible threshold concentration and 24 hour TWA during fumigation and aeration. During aeration, an additional exclusion zone set up 20 m from the exhaust fan vent also ensured that worker and bystander exposure to SF was well below the permissible threshold concentration and 24 hour TWA of 3 ppm. The size of the exclusion zone from the aeration fan, particularly down wind and down air stream, may vary based on concentration of fumigant in the bunker at initiation of aeration, aeration fan capacity, wind speed, and other conditions. An SF clearance detector, such as the SF-ExplorIR, can delineate the appropriate boundaries from the aeration fan for excluding personnel during aeration. This monitoring is required by labeling for ProFume as follows; "The perimeter of the fumigation area, especially downwind, must be monitored to ensure that ProFume concentrations are kept within acceptable levels outside the fumigation area."

These data from this trial indicate that if both the prescribed exclusion zone of 3 m and label directions for ProFume are observed, bystander and worker exposure to SF concentrations will not exceed permissible levels. Dow AgroSciences is currently undertaking work in order to expand the usage of ProFume into new stored produce in order for these industries to remain viable under the threat of insect resistance and withdrawal of methyl bromide.

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