Comparison the effectiveness of the fumigants sulfuryl fluoride and phosphine in controlling warehouse pest insects

N Subekti* and M A Syahadan
Biology Department, Faculty of Mathematics and Natural Sciences, State University of Semarang, Semarang, Indonesia

*Corresponding author: nikensubekti@mail.unnes.ac.id

Abstract. Warehouse pest insects contained in commodities can affect the quality and quantity of the commodity. Every industry which has a commodity stored in warehouses makes efforts to prevent damage to the commodity. Control of insect pests during storage is generally conducted by fumigations with phosphine (PH$_3$) and sulfuryl fluoride (SO$_2$F$_2$). This study aims to analyze and compare sulfuryl fluoride and phosphine fumigants in controlling pest insects in the animal feed industry warehouses in Semarang, Central Java. The test insects used are all kinds of insects found on piles of commodities that will be fumigated. The test used is the mortality test. Observations are carried out before and after fumigation takes place. The one-way ANOVA with the Tukey follow-up test was employed to analyze the data. There was a difference in the average mortality of warehouse pest insects between treatments and the highest mortality rate in fumigation using sulfuryl fluoride. Thus, fumigants sulfuryl fluoride and phosphine can affect the mortality of warehouse pest insects. Fumigation using sulfuryl fluoride is easy to apply, more effective, and exposure time is faster compared to phosphine.

1. Introduction
Before commodities reach the hands of consumers, they usually experience storage conditions. During the storage of commodities can be attacked by warehouse pests. Insects generally damage stored products by eating them directly [1]. The metabolism of warehouse pest insects can cause an increase in temperature and humidity in commodities so that fungi can grow and seed germination occurs [2]. Thus, it causes contamination and economic loss by reducing the quality and quantity of commodities in storage [3]. Warehouse pest insects can cause heavy loss of commodities by 34% - 40% [4]. Heavy loss of commodities due to the ones of warehouse pest insects continues to increase daily for certain environmental conditions and factors [5]. It is estimated that economic losses due to warehouse pest insects make up 9 percent of the total products stored in developed countries. In developing countries, the economic losses amount to more than 20% of the total products stored [6]. *Alphitobius diaperinus* and *Tribolium castaneum* Herbst are considered the main pests of stash products globally, including animal feed [7].

*Alphitobius diaperinus*, better known as Frenki fleas, are insect pests in poultry and animal feed [8]. These insects undergo a complete metamorphosis of eggs in its life cycle then become larvae, pupeae, and adult fleas. Adult fleas can live between 3 - 12 months. Eggs hatch within 4 to 7 days and become adult beetles again after 40-100 days, depending on food reserves and temperature [9]. These pests serve as vectors of pathogens, especially bacteria, protozoa, and viruses. These pests serve as...
vectors of pathogens, especially bacteria, protozoa, and viruses. If contaminated animal feed *Alphitobius diaperinus* is eaten by poultry, it can cause disease and affect poultry's weight [10].

*Tribolium castaneum* Herbst, better known as the red flour beetle, is one of the tropics' most important species. Female beetles lay eggs between grains of flour, randomly. Eggs stick to the flour and are protected by particle flour. Female beetles can lay eggs of up to 1000 eggs during their lifetime. The average egg production per parent reaches 450 grains. A few days later, the eggs hatched. Larvae move actively using all three pairs of limbs. During its growth, larvae undergo skin changes 6-11 times (an average of 6-7 times). At total growth, the larva reaches a length of 8-11 mm. By the time the cocoon of larvae rises to the surface of the material and cocoons without making the coke first with the position of lying on its back. Pupae can be found among commodities attacked without being protected by coke. The phase of eggs and pupae is relatively short. More than 60% of its life cycle is spent as larvae. These beetles can breed year-round in warm areas. The life cycle takes 40 to 90 days, and adult insects can live for three years. These insects are the most common insects found in storage sheds. Severely stricken feed materials are usually contaminated by benzoquinone (excretion of *T. castaneum*), making it unfit for consumption [11].

A common control used to deal with insect pests in storage warehouses is fumigation. Fumigation is the process of pest control in commodities using certain fumigants, in airtight spaces, at certain temperatures and pressures. Fumigant is a type of pesticide that in certain temperatures and pressures in the form of gases and in certain concentrations and times can kill pests (disruptive organisms). Fumigants commonly used for the fumigation of warehouse pest insects are sulfuryl fluoride and phosphine [12].

Sulfuryl fluoride (SF) is an inorganic chemical consisting of 99% S0\_2F\_2 and 1% of additional ingredients. SF is inorganic, non-organic, and non-reactive to commodities to be fumigated. Thus, making it a potentially better penetrator. SF is not flammable and has no flashpoint. In dry conditions can be stable up to 400 °C. However, temperatures exceeding 400 °C SF will be degraded into hydrogen fluoride (HF) and sulfur dioxide. When combined with moisture, these chemicals can form weak acids that can stain the surface of fumigated commodities. SF has a very low boiling point of -55.2 °C at 760 mm Hg and has a very high vapor pressure of 17.7 mm Hg at 25 °C. SF is odorless and colorless. Thus, a small amount of chloropicrin is generally mixed with this fumigant to warn of its potential dangers, especially fumigators [13].

Meanwhile, phosphine is a highly toxic compound, odorless, colorless, and has no taste in fumigated commodities. Phosphine is highly flammable and has flashpoints at concentrations above 1.8% in the air or 25 g/m\(^3\) at normal air pressure. It is explosive if exposed to water and at temperatures over 100 °C flammable by itself. Phosphine is highly reactive with materials made of copper/precious metals can cause corrosion [14].

2. **Methods**

2.1 **preparation of test insects**

Sampling is carried out before the fumigation process takes place. All living insects caught in piles of commodities to be fumigated are counted in numbers and grouped by type to be used as test insect samples. Based on calculations using Federer's formula, the number of test sample points for each treatment amounted to 16, resulting in a total of 32 test sample points. Test sampling was conducted at 32 points in the animal feed industry warehouse in Semarang, Central Java, Indonesia. The type and number of insects used for experimentation at each point depending on live insects caught on piles of commodities to be fumigated.

2.2 **Fumigation applications [15-16]**

The fumigation carried out in this study is part of routine measures of pest insect control in animal feed storage warehouses. Before each fumigation, commodity piles are cleaned and sealed following the agricultural quarantine agency's fumigation treatment standards. All fumigation is carried out
between January and February 2020. The exposure period is defined as the time between the first release of the fumigant and the beginning of the seal release. Animal feed commodities to be fumigated are stacked in such a way that proper gas distribution is obtained. The exposure period is determined based on the agricultural quarantine agency's fumigation treatment standards, which lasts 1x24 hours for sulfuryl fluoride and 3x24 hours for phosphine. The amount of fumigants used is calculated based on the dosage and amount of commodities to be fumigated, taking into account various fumigation conditions such as estimated leak rate (half-loss time or HLT), duration of exposure, temperature, and target pest.

2.3 Identification and calculation of mortality
After fumigation, observation of the mortality of test insects and each fumigation point's location is marked using GPS. After that, put in a plastic ziplock. To identify each type in Biology Laboratory, Faculty of Mathematics and Natural Sciences, Semarang State University. Observations for fumigation with sulfuryl fluoride were conducted after 1x24 hours exposure time and 3x24 hours for phosphine. One-way ANOVA analysis and Tukey tests are involved in analyzing the data.

3. Results and discussion
The activities of sulfuryl fluoride and phosphine fumigants are tested against warehouse pest insects. It is visible after 1x24 hours of exposure time for sulfury fluoride and 3x24 hours for phosphine. It is characterized by a mortality test of pest insects.

![Figure 1. Mortality number Alphitobius diaperinus and Tribolium castaneum herbst.](image)

The highest mortality in fumigation treatment was sulfuryl fluoride, with an average mortality rate of 95% with an exposure time of 1x24 hours. Meanwhile, fumigation with phosphine takes 3x24 hours of exposure to achieve an average mortality value of 78%, as for the types of warehouse pest insects that attack stored commodities vary. The types of insects found are Alphitobius diaperinus and Tribolium castaneum Herbst. Based on this study, the frequency of T. castaneum attacks reached 72% of all test points. Based on the description above T. castaneum is one of the important insects in tropical areas, including Indonesia. These insects are found in storage warehouses and become the main pests that damage commodities.

ANOVA's one-way test results showed a variation in the treatment of the average mortality value of warehouse pest insects with a P-value of 0.000 < 0.05. Phosphine works through the inhibition of the cell respiration process. Phosphine toxicity is associated with oxidant-free radicals and inhibition of metabolic enzymes, such as cytochrome c oxidase. The production of free radicals exceeds that of antioxidant capabilities intracellular to neutralize it is very likely to cause cell damage. Often, this damage is referred to as oxidative damage. Oxidative damage caused by free radicals has implications for various pathological conditions and can lead to death [17]. Lower concentrations with longer exposure
times are rated more effective for controlling warehouse pest insects [18]. While Sulfuryl fluoride has a more complex way of working, it enters insects' bodies through spiracles. Sulfuryl fluoride in the body of insects will decompose into fluoride and sulfate. Fluoride ions prevent fat metabolism by disrupting glycolysis cycles in insects needed to maintain energy adequacy in survival. Fluoride ions can inhibit oxygen uptake, disrupt the normal balance of phosphate, and inhibit hydrolysis (breakdown) of fatty acids. Fluoride ions in sulfuryl fluoride are thought to bind to calcium, potassium, and magnesium. Enzymes that require magnesium ions for normal function are inhibited by sulfuryl fluoride. The disturbance caused insects to be forced to use proteins and amino acids as alternative energy sources without being followed by increased metabolism due to reduced oxygen supply, thus reducing the metabolic energy required by insects resulting in death [19].

Phosphine has the advantage of being cheaper than sulfuryl fluoride and leaves no residue on fumigated commodities. Thus, many companies that store their commodities in storage warehouses use phosphine to control warehouse pests. However, its inappropriate application, such as the use of inappropriate dosages, causes some adverse effects. Insect resistance to phosphine has occurred in several countries in the world, such as the Americas [20], Australia [18], and including Indonesia [21]. The highest resistance occurs in the pupa phase, followed by imago, and the lowest in the larvae. In general, the time of exposure takes phosphine to kill pest insects for 3 x 24 hours. However, based on some previous descriptions of resistance to phosphine. If the original frequency of resistant insects increases n times, then exposure needs to be extended, at most n days, to reach the same level of insect control [22]. Thus, exposure needed to kill pest insects can be more than 3 x 24 hours. Repeated use of phosphine can result in residues in commodities. Besides, the environment in which fumigation is carried out using phosphine should be taken into account. Because this compound is reactive and explosive if exposed to water.

Sulfuryl fluoride is effective for controlling insects found in storage warehouses in all phases of life. Fumigation with sulfuryl fluoride proved effective for controlling warehouse pest insects resistant to phosphine [23]. The time of exposure required for fumigation using sulfuryl fluoride depends on the biological activity of molecules reaching the target site inside pest insects and on the duration of gas exposure. It generally takes 1 x 24 hours. Sulfuryl fluoride has high penetration power, is not reactive to commodities. Thus, it is very easy to apply. Temperature is one of the important factors in fumigation to turn off insect pests. The temperature trend in Indonesia generally increases from 0.03 – 0.9 °C. Thus, it is very supportive of the application of sulfuryl fluoride. In addition, sulfuryl fluoride is more stable against ozone and does not react with active atmospheric radicals making it safe for the environment [24]. However, the use of sulfuryl fluoride to control warehouse pest insects in food commodities can leave inorganic fluoride residues, and these residues can cause serious health problems.

Phosphine has the advantage of being cheaper than sulfuryl fluoride and leaves no residue on fumigated commodities. Suppose the contaminated animal feed is consumed by farm animals and consumed by humans. Thus, it can cause serious health problems. This fumigant is also easily absorbed by human skin, which will cause edema in the lungs [25]. Suppose both sulfuryl fluoride and phosphine gases are decomposed in the air and inhaled by fumigation workers. In that case, it can cause respiratory disturbances, irritation, nausea, abdominal pain, depression of the central nervous system, slowing speech, and numbness [26].

4. Conclusion
Fumigants sulfuryl fluoride and phosphine affect the mortality number of warehouse pest insects. The most effective fumigant is sulfuryl fluoride. Fumigation using sulfuryl fluoride with an exposure time of 1x24 hours led to the highest average mortality of warehouse pest insects. Therefore, sulfuryl fluoride should be considered as a fumigant for controlling warehouse pest insects.
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