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## STUDY OF ALUMINUM PHOSPHIDE LEVELS IN WASTE FUMIGANTS FROM FOOD SHIPMENTS FOLLOWING SIMPLE IMMERSION TREATMENT

Increasing concentrations of aluminum phosphide (AIP) in waste fumigants and residues pose a serious threat to human health. This study focused on the effectiveness of the widely used simple immersion treatment for waste fumigants from shipments, which usually have a higher concentration of residual AIP. A field survey of an operational process was conducted followed by a quantitative analysis of the immersion treatment's hydrolytic effect on AIP. Further investigation on the safety of waste fumigants after the immersion treatment was conducted. It was found that the AIP concentration in the waste fumigant varied significantly with the sampling date, ranging from 12.93±0.67 wt. % to 29.50±1.18 wt. %. Simple immersion treatment could reduce the concentration of residual AIP in waste fumigants but the hydrolytic effect varied largely ranging from 19.5% to 31.9%. The concentration of residual AIP remained high (9.1–20.1 wt. %) after the immersion treatment. About 3.2–15.2 wt. % of AIP remained in the samples, following an additional 40 days of natural air-drying when phosphine gas release was not detected. The study indicates that conventional simple immersion treatment cannot ensure the complete hydrolysis of AIP from waste fumigants of shipments.

### 1. INTRODUCTION

The development of global economy and expansion in international trade have resulted in the extensive usage of chemical fumigants in the import and export of agricultural products in order to meet the quarantine requirements of importing countries and pest and disease control during long-distance freight transport. Aluminum phosphide (AIP) is currently the most common chemical for pest control of stored foods in most

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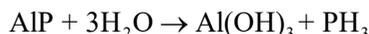
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countries [1, 2] and is regarded inexpensive and effective. Consequently, AIP fumigants are transported across various countries along with foodstuff [3-5].

However, abundant fumigants are wasted when the temperature is low or transport distance is short. These waste fumigants residues are mainly composed of AIP and its hydrolytic products [6,7] such as aluminum oxide, etc., which are highly toxic inorganic compounds mainly because of AIP. It can release phosphine (PH<sub>3</sub>) gas on contact with either moisture or acid in the environment, as shown in the following chemical reaction:



PH<sub>3</sub> is a colorless gas at room temperature under atmospheric pressure. Additionally, pure PH<sub>3</sub> is odorless at concentrations up to 282 mg·m<sup>-3</sup> which are highly toxic. The autoignition temperature of pure PH<sub>3</sub> is 38 °C but the presence of impurities, particularly diphosphine (PH<sub>2</sub>-PH<sub>2</sub>), often causes the reacting product to ignite spontaneously at room temperature and form explosive mixtures with air at concentrations greater than 1.8% [2]. Thus, the AIP presence has a significant effect on the safety of waste fumigant residues, and can be hazardous to humans, animals, and the environment if not handled properly [8, 9]. However limited researches have focused on it.

In recent years, several safety accidents caused by improper handling of AIP fumigant residues have been reported posing a substantial risk to the health of food inspection and quarantine personnel, as well as food safety [8, 10, 11]. Hence, there is an urgent need to identify suitable methods for handling waste fumigants to ensure smooth workflow during the inspection and quarantine of imported foodstuff and guarantee steady progress in food safety strategy.

Generally, domestic and foreign treatment methods for waste fumigants mainly include burial or incineration [12, 13]. However, with increasing urbanization and scarcity of land resources risk of residue leakage, spilling, and water contamination caused by traditional deep burial treatment is high. Equipment requirements for incineration are substantial and need to be set up in close proximity, resulting in higher costs and operational difficulties. Additionally, waste fumigants produced during shipping exhibit higher fluctuating concentrations of residual AIP, compared to waste fumigants generated by ordinary food storage increasing the risks of these techniques [8, 11, 14]. Furthermore, due to differences in temperature and duration of food storage, waste fumigants two to five times the volume of the original fumigant, containing undecomposed AIP (3–30 wt. %) are produced [8, 9, 14, 15]. According to data published by the General Administration of Customs, the preliminary estimate of waste fumigants produced by the shipping of food was more than 300 t in 2015. Therefore, simple conventional fumigant burial or incineration techniques are no longer applicable and specific pre-treatment of waste fumigants before their safe disposal is required.

Immersion hydrolysis treatment is currently used to treat waste fumigants of shipments [11–13]. The danger of waste fumigants mainly arises from non-hydrolyzed AIP.

As AIP is easily hydrolyzed treatment solutions such as water, detergent water, acid and alkali solutions are added to promote the degradation of unreacted AIP in the residues [4, 11]. This method is simple, convenient, and easy for project implementation. However, research in this field is limited and quantitative analyses investigating the effects of the AIP degradation and its safety are lacking.

In this study, an actual project using immersion treatment to process waste fumigants was used as a case study. Samples were randomly selected between March to November 2015 and the hydrolytic effect of immersion treatment on AIP levels was investigated. In addition, concentrations of AIP and phosphorus in the hydrolytic residues obtained after air-drying for 40 days were investigated, to analyze the safety of waste fumigants following the immersion treatment.

## 2. MATERIALS AND METHODS

*Field survey of case study.* Samples were obtained from an operational project that used immersion treatment for waste fumigants in Zhoushan, China. The handling capacity of this project was 50 t/year. The site occupied an enclosed area of around 1000 m<sup>2</sup>, and included temporary storage, processing, and natural air-drying areas. The 300 m<sup>2</sup> main processing area used a simple detergent solution for immersion treatment to process waste fumigants. The process flow of the project is shown in Fig. 1. Around 65% of the immersion pool was filled with water and detergent equivalent to 3 wt. % of the residue mass was added. After ensuring the safety of the surrounding environment, packaging containing waste fumigants obtained directly from a shipment was placed in the exposed immersion pool and PH<sub>3</sub> gas produced during decomposition was allowed to diffuse freely. At the end of the treatment, the residues were removed from the pool and air-dried naturally. They were stacked randomly on the ground without cover until PH<sub>3</sub> gas was not detected (usually about 40 days). Then, the residues were subject to deep burial treatment.

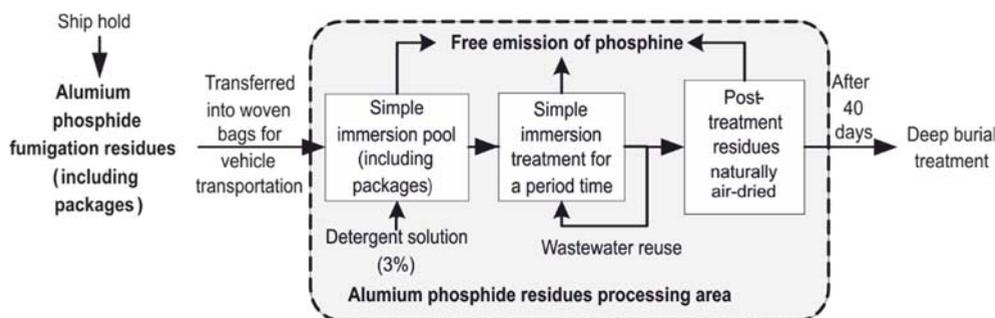


Fig 1. Process flow of simple immersion treatment of waste fumigants in the case study

The treated waste AIP residues were solid pills used for grain fumigation during long-distance freight ship transport. Once the grain had been loaded into the cargo hold, it was treated with AIP pills placed on the surface of the grain piles in each hold. Nearly 1–1.5 g of AIP was used per m<sup>3</sup> of storage. The large quantity of AIP products reacted when they came in contact with the air, water, or moisture to release PH<sub>3</sub> gas thereby killing insects and larva. Therefore, some unreacted AIP and its hydrolytic products such as aluminum hydroxide remained in the waste residual. The specific contents of these components differ between different waste fumigants, but the main hazardous component is AIP.

*Sample collection.* Samples between 100 g and 200 g were randomly collected for investigation from March to November in 2015. They were packed in sterile glass vials, sealed, and sent to the laboratory for testing. Each sample was obtained by mixing three repeats from each sampling point. Basic information about the samples collected is shown in Table 1.

Table 1

Basic information on randomly collected samples

Sampling date (average temperature)	Sample category	Sampling point	Sample weight [g]
March 2015 (16.5 °C)	original	3	150
	air-dried	3	100
July 2015 (29.2 °C)	original	4	200
	hydrolyzed	3	180
	air-dried	3	100
August 2015 (32.0 °C)	original	4	200
	hydrolyzed	3	150
	air-dried	4	120
November 2015 (12.4 °C)	original	3	160
	hydrolyzed	3	150
	air-dried	4	100

Original sample: fresh sample obtained from the ship, i.e. input sample for immersion treatment. Hydrolyzed sample: sampling after immersion treatment, i.e., output sample. Air-dried sample: output sample after 40 day of air-drying, i.e., sample considered safe for land filling with phosphine gas not detectable. In March, as the immersion pool had been empty for about 10 days on the sampling day, the hydrolyzed sample, i.e., output sample after immersion treatment could not be obtained

*Detection indices and method.* Testing indicators were residual AIP, total phosphorus, and total nitrogen concentrations. AIP concentration was determined using the specified titration method [16]. Well-mixed residue powder was treated with sulfuric acid to release PH<sub>3</sub> and treated with potassium permanganate solution for oxygen absorption.

Subsequently, oxalic acid was added and back-titrated with potassium permanganate. Potassium permanganate consumed was recorded and the concentration of AIP was calculated [16]. Based on this, the hydrolytic rate of residual AIP was calculated using the equation

$$\text{Hydrolytic rate} = \frac{C(\text{AIP})_{\text{OS}} - C(\text{AIP})_{\text{HS}}}{C(\text{AIP})_{\text{OS}}} \times 100\% \quad (1)$$

where  $C(\text{AIP})_{\text{OS}}$  is the AIP content in original samples; and  $C(\text{AIP})_{\text{HS}}$  is the AIP content in hydrolyzed samples. Additionally, the activity level of waste fumigant was expressed as the AIP content of waste fumigant divided by the AIP content of fumigant product (56 wt. %).

Total phosphorus and nitrogen levels were determined by the spectrophotometric method. After the residues underwent successive heated digestion using aqua regia, hydrofluoric acid, and perchloric acid on an electric hot plate, the resulting solution was loaded onto 0.22  $\mu\text{m}$  microporous membrane to remove the impurities which could not digest, and then measured according to the existing standards [17, 18].

*Statistical analysis.* Mean values and standard deviation of the data were analyzed using Excel (Microsoft, 2007, USA) and OriginPro7.5 (OriginPro 7.5, OriginLab Corporation, Northampton, USA). Significant differences were determined using Fisher's Least Significant Difference (LSD) test at  $p < 0.05$  level.

### 3. RESULTS AND DISCUSSION

#### 3.1. CONCENTRATION OF AIP IN WASTE FUMIGANT

The concentration of AIP in the original samples varied significantly with the sampling date ranging from  $12.93 \pm 0.67$  wt. % to  $29.50 \pm 1.18$  wt. %, except during July and August ( $p > 0.05$ ) (Fig. 2). Compared to the content of AIP in the product (56 wt. %), the level of activity in residues reached 23–53%. This was mainly due to factors such as differences in weather and the length of fumigation use (the length of time in freight) [8].

Compared with the AIP content in the waste fumigants produced by ordinary food storage (3–10 wt. %) [10, 11], the concentration of AIP in fumigant residues generated in shipments was higher, resulting in a high risk from these types of residues. The residues can produce highly toxic  $\text{PH}_3$  if disposed poorly, and come in contact with water [8, 19, 20]. The concentration of AIP in fumigant residues showed significant difference at various sampling temperatures and was low during hotter months and high during cooler months. This indicates that the AIP content in waste fumigants exhibits seasonal variation to a certain extent. Therefore, with humid climate in winter, safe storage of fumigant residues before their final disposal is very important.

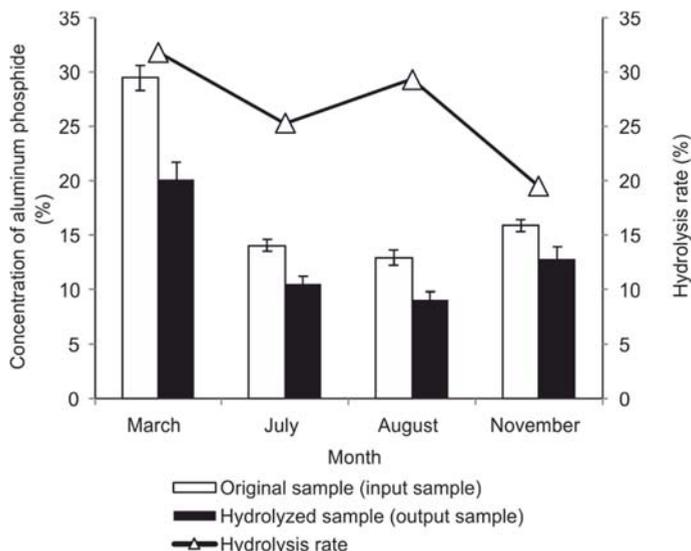


Fig 2. Content of AIP in original and hydrolyzed samples

### 3.2. HYDROLYTIC EFFECT OF IMMERSION TREATMENT ON AIP

The hydrolytic effect was analyzed by comparing changes in the concentration of AIP in the original samples with hydrolyzed samples as shown in Fig. 2. The results showed that the concentration of AIP in the waste fumigants decreased significantly after the immersion process. However, the hydrolysis rate varied in various batches ranging from 19.5 to 31.9%. The hydrolytic effect was highest in March when the concentration of AIP decreased from 29.5 to 20.1 wt. %. In contrast, hydrolytic effect in November was the lowest as the concentration of AIP decreased from 15.9 to 12.8 wt. % only. The decrease in the concentration of AIP during July and August was moderate. This was probably due to low concentration of AIP in the input samples as temperature was higher during July and August as shown in Table 1. Moreover, artificial stirring to promote hydrolysis was not carried out during these months. However, as the concentration of AIP was higher in the input samples during March and November, certain degree of artificial stirring was performed to accelerate the hydrolysis. Therefore, the hydrolytic effect difference was mainly because of the AIP concentration in the input samples as well as technical parameters such as reaction temperature etc.

Furthermore, although the hydrolytic effect was the highest in March, the concentration of residual AIP was still high at 20.1 wt. %. From July to November, the concentrations of AIP in the output samples were also considerably high ranging from 9.1 to 12.8 wt. %. These levels threaten the safe disposal of residues even after the immersion treatment.

### 3.3. SAFETY ANALYSIS OF WASTE FUMIGANT AFTER IMMERSION TREATMENT

Although immersion treatment reduced the concentration of AIP to some extent, the concentration after treatment was still considerably high ranging from 9.1 to 20.1 wt. % posing a hazard during deep burial. Hence, further processing of the waste fumigants was investigated. The residues obtained after immersion treatment were air-dried for 40 days, and the residual amounts of AIP, total phosphorus, total nitrogen, and their variation patterns were studied. The results are shown in Table 2.

Table 2

Test results of relevant indicators for air-dried waste fumigants

Sampling date	Stirring degree	Concentration of AIP [wt. %]	Total phosphorus (TP) [mg/g]	Total nitrogen (TN) [mg/g]
March 2015	artificial	15.17	44.17	0.11
July 2015	no	6.19	22.91	0.18
August 2015	no	3.21	16.18	0.23
November 2015	artificial	7.60	24.17	0.15

Air-dried samples considered completely treated ( $\text{PH}_3$  gas was not detectable) still contained 3.2–15.2 wt. % of AIP. This was mainly due to continuous increase in pH during hydrolysis, which caused the precipitation of aluminum hydroxide. These formed partial inclusions over AIP particles, and combined with the stationary state of the solution, led to poorer exposure of AIP to the solution. This eventually resulted in a large amount of residual AIP in the solution. However, the concentration of nitrogen in the AIP residues was very low and there was almost no discrepancy. This indicated that the focus should be on AIP and phosphorus levels during the course of subsequent disposal.

Graver and Whittle [9] found that even after 19 months of deep burial of the waste fumigants, up to 4.1% of the toxic  $\text{PH}_3$  gas could be released. This suggests that the simple immersion treatment employed in this study cannot guarantee complete hydrolysis of the fumigant residues. Currently, simple immersion treatment and deep burial techniques that are widely used in China pose a large risk to the environment and human health. Developing effective technologies for the detoxification of waste fumigants through decomposition or hydrolysis of AIP are needed to ensure that processed residues can meet the safety standards of landfills.

## 4. CONCLUSION

A field survey of an operational project that utilized simple immersion treatment for waste fumigants from shipments has been conducted. The results showed that simple immersion treatment could reduce the concentration of residual AIP in waste fumigants

but the hydrolytic effect showed considerable variation among different samples ranging from 19.5% to 31.9%. Moreover, the concentration of residual AIP following immersion treatment remained relatively high ranging from 9.1% to 20.1%. Even after 40 days of natural air-drying, when the release of PH<sub>3</sub> gas was not detected, 3.21–15.17 wt. % of AIP remained in the samples. This indicates that simple immersion treatment employed in this study could not guarantee the complete hydrolysis of the fumigant residues.

These results provide a single example of effects of simple immersion treatment on AIP degradation that was dependent on the sample contents and treatment temperature. Evidently, more research is required to determine whether the content of the active ingredient can be reduced below the levels of landfill standards using improvements in immersion technology or adopting other effective technologies.

#### ACKNOWLEDGEMENTS

This work was supported by the science and technology project funded by the General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (2016IK288), the Open Foundation of Key Laboratory for Solid Waste Management and Environment Safety (Tsinghua University), Ministry of Education of China, Beijing 100084, China (No. SWMES 2015-07).

#### REFERENCES

- [1] SCHMIDT E.L., JUZWIK J., SCHNEIDER B., *Sulfuryl fluoride fumigation of red oak logs eradicates the oak wilt fungus*, Eur. J. Wood Wood Prod., 1997, 55, 315–318.
- [2] PANT H., TRIPATHI S., *Fumigation of wood with aluminium phosphide for protection against fungi*, J. Trop. For. Sci., 2011, 23 (4), 363–370.
- [3] HANSEN H.L., PEDERSEN G., *Poisoning at sea. Injuries caused by chemicals aboard Danish merchant ships 1988–1996*, J. Toxicol. Clin. Toxicol., 2001, 39 (1), 21–26.
- [4] MUSSHOF F., PREUSS J., LIGNITZ E., MADEA B., *A gas chromatographic analysis of phosphine in biological material in a case of suicide*, Forensic. Sci. Int., 2008, 177 (2–3), 35–38.
- [5] PHILLIPS T.W., THOMS E.M., DEMARK J., WALSE S., *Fumigation* [In:] D.W. Hagstrum, T.W. Phillips, G. Cuperus (Eds.), *Stored Product Protection*, Kansas State University. Manhattan, KS, 2012, 157.
- [6] BANKS H.J., *A continuous cumulative procedure for analysis of phosphine*, J. Stored Prod. Res., 1987, 23, 213–221.
- [7] Degesch, *Material safety data sheet. Spent Degesch aluminium phosphide products*, Degesch America, Inc., Weyers Cave, VA 24486 USA, 2000, 4.
- [8] LODDÉ B., LUCAS D., LETORT J.M., JEGADEN D., POUAGNET R., DEWITTE J.D., *Acute phosphine poisoning on board a bulk carrier. Analysis of factors leading to a fatal case*, J. Occup. Med. Toxicol., 2015, 10, 10.
- [9] GRAVER J.V.S., WHITTLE C.P., *Phosphine residues remaining in aluminium phosphide preparations after burial*, Phytoparasitica, 2001, supplement.
- [10] FINKELMAN S., NAVARRO S., NAVARRO H., ASHBELL G., GLASER U., *Fumigation of fresh herbs with phosphine as a new quarantine treatment*, IOBC/WPRS Bull., 2012, 81, 193–197.
- [11] ZHAO Y., ABBAR S., PHILLIPS T.W., SCHILLING M.W., *Phosphine fumigation and residues in dry-cured ham in commercial applications*, Meat Sci., 2015, 17, 57–63.
- [12] CASA B., *Application procedures for Gastoxin® tablets and Gastoxin® pellets*, Casa Bernardo, Samaritá, 11346-300 São Vicente/SP, Brazil, 2000, <<http://www.casabernardo.com.br/manutp.html>>.

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- [13] Degesch, *Applicator's manual for Degesch Phostoxin® Pellets and Tablets*, R. Degesch America Inc., Weyers Cave, VA 24486, USA, 1999, 21–22.
- [14] BRUCE R.B., ROBBINS A.J., TUFT T.O., *Fumigant residues, phosphine residues from phostoxin-treated grain*, J. Agric. Food Chem., 1962, 10 (1), 18–21.
- [15] CHEN C., HU X.J., ZHANG L.L., LI C.B., BI W.Y., MA M.P., *The study on the determination of deliquescence velocity of aluminum phosphide pills and its application*, J. Henan Univ. Techn., Nat. Sci. Ed., 2015, 36 (3), 81–85.
- [16] AQSIQ, *56% Aluminium phosphide tablets (GB 5452-2001)*, General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (AQSIQ), Beijing 2010.
- [17] AQSIQ, *Water quality. Determination of total phosphorus. Ammonium molybdate spectrophotometric method (GB 11893-89)*, General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China (AQSIQ), Beijing 1989.
- [18] MEP, *Water quality, Determination of total nitrogen. Alkaline potassium persulfate digestion UV spectrophotometric method (HJ 636-2012)*, Ministry of Environmental Protection of the People's Republic of China (MEP), Beijing 2012.
- [19] PESHIN S.S., SRIVASTAVA A., HALDER N., GUPTA Y.K., *Pesticide poisoning trend analysis of 13 years. A retrospective study based on telephone calls at the National Poisons Information Centre, All India Institute of Medical Sciences, New Delhi*, J. Forensic. Leg. Med., 2014, 22, 57–61.
- [20] RAIZADA A., KALRA O.P., KHAIRA A., YADAV A., *Profile of hospital admissions following acute poisoning from a major teaching hospital in North India*, Trop Doct., 2012, 42 (2), 70–73.