The Influence of Plastic Consumer Packaging for Polished Rice on Phosphine Gas Penetration, Desorption, and Residue

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Abstract: Phosphine fumigation of polished rice within polyethylene consumer packaging was carried out, and the effects of plastic film on gas penetration into the package, gas desorption from the package, and phosphine residue on fumigated polished rice were investigated. 100% mortality was obtained for the Tribolium confusum adults and Plodia interpunctella larvae that were inserted into the center of the package containing 2kg of rice that was then fumigated with PH3 at 0.82 g/m² for 72 hours at 15°C. A certain amount of phosphine gas that can completely kill test insects should be able to penetrate into the center of consumer packaging through polyethylene film. As for gas desorption, gas concentrations inside packages without ventilation holes remained higher than packaging with 14 holes. Gas concentrations inside packages without holes were from 519ppm at 10 minutes through 59ppm at 72 hours after forced exhaust was completed. For the package with 14 holes, detected concentration was rapidly decreased to ca. 20ppm at the 24-hour point, and after the 48-hour point all values were indicated below 1ppm. Rice in packages identical to those used in the desorption study were also analyzed for phosphine residue by headspace gas chromatography. Actual levels of residue in the package without holes were from 0.0011 to 0.0014ppm, not prominently higher values compared to residues acquired in analysis of the package with 14 holes, which were detected from 0.0009 to 0.0011ppm; therefore, it is considered that ventilation holes are not a main factor impacting residue levels. Regardless of the number of holes in a package, all residues were indicated at a much lower level than the maximum residue limits (MRL), set at 0.1ppm for rice in Japan. Longer-term aeration should be recommended to expedite gas desorption from rice packages to ensure worker safety.

Key words: Phosphine fumigation, penetration, desorption, residue, packaged rice

Introduction

Japan imports various kinds of agricultural products from overseas. In recent years, however, the worldwide trend in Japanese food and the advancement of income levels in Asian countries are considered good opportunities for the export of high-quality agricultural products from Japan. This is one of the important policies for implementing the so-called offensive agricultural administration, and strategic approaches are being undertaken to promote exports (MAFF, 2005). The annual consumption of rice per person was 111 kg of polished rice in 1965, but it has been constantly decreasing to only 61 kg in 2006 in the context of changing tastes and other factors. Conversely, the acreage of rice cultivation has not been favorably reduced pursuant to the national government’s reduction plan; accordingly, the annual production of rice in 2007 was surplus to Japan’s requirements (MAFF, 2008). Although Japanese rice has already been exported to Taiwan, Hong Kong, Singapore, and other countries, further expansion of exports is desirable (MAFF, 2008). On the other hand, changing tastes for agricultural products could recently be diversifying their transportation, markets, and forms. In particular, it is expected that Japanese rice should be exported in the form of consumer package for reasons of efficient distribution and transportation in foreign countries. Such consumer packaging is usually made of plastic (e.g. polyethylene, polypropylene, etc.) owing to its ability to preserve food, the ability to print alluring labels on the package, and other commercial reasons. Phytosanitary measures, for instance fumigation, are often adopted in the import and export quarantine system when quarantine insect pests are found at inspection by the National Plant Protection Organizations (NPPO).

Gas penetration in stacks of milled rice in 100-lb. woven polypropylene bags was investigated, and good penetration

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was obtained (COGBURN, 1974). The form of plastic packaging is different from sack and/or bag (i.e. hemp bags or woven plastic bags) that are regularly used in international grain transportation, gas permeability of plastic packaging was considered to be quite low. Regarding the fumigation of grain in plastic consumer packaging as it is, fumigation efficacy should be confirmed if it is unclear whether fumigant gases can sufficiently penetrate into plastic packaging. Methyl bromide has a wide spectrum as a fumigant and has been used effectively in the quarantine system for a long time; it was listed in an ozone-depleting substances, however, and its usage has been restricted (UNEP, 2006). Phosphine or aluminum phosphide tablets have been widely adopted for grain fumigation and have also been studied extensively, such as for the fumigant’s properties and effects against stored-product insects (LIN, 1981; MORI and KAWAMOTO, 1966; RAJENDRAN et al., 2001; TATEYA et al., 1974). It is also used for the fumigation of brown rice in transit based on the property that it requires a longer exposure time (SCHESSER, 1977) and complete mortality for several kinds of stored-product insect pests is provided (MOLINARI et al., 1993). The sorption of phosphine to brown rice is reported to be lower (SOMA et al., 1996), which means a swift desorption from the rice in packaging and relatively low residue may be expected. For that reason, phosphine must be appropriate for rice-package fumigation among the registered fumigants in Japan for securing both quarantine security and food safety.

We conducted phosphine fumigation using Japanese polished rice within plastic consumer packaging and investigated the influence of gas penetration into plastic packaging, gas desorption from packaging, and phosphine residue in the rice.

Materials and Methods

I. Gas penetration test

To confirm gas penetration into consumer packaging, we conducted a substitute fumigation test by inserting test insect pests into the center of a plastic package filled with 2kg of polished rice and evaluated their mortality after fumigation, instead of monitoring gas inside the package using a sampling tube. Test insects were used as an indicator of gas penetration. The degree of phosphine gas penetration into the package was determined by the mortality of the tested insects.

(a) Test insects
Confused flour beetle (Tribolium confusum), adult
Indian meal moth (Plodia interpunctella), larva

Both test insects used have been reared for successive generations for more than 15 years at the Research Division of the Plant Protection Station at Yokohama City in Japan.

(b) Test rice
Polished rice (Niigata Prefecture brand, harvested in 2007) processed at the Kanagawa factory of JA Pearl Rice Eastern Japan Corp.

(c) Test plastic packaging
Polyethylene consumer package for polished rice: size: 34.8×23.8 cm; thickness: 70–80 µm; oxygen permeability rate1 >2000 ml/m² atm·24 h; bag for 2kg of rice with 6 pinholes on the upper side for ventilation (Fig. 1). Kanagawa factory of JA Pearl Rice Eastern Japan Corp.

(d) Fumigation

A few stainless steel mesh cages that confined fixed numbers of the two test insect species separately were inserted into the center of consumer packages through a pipe using a plunger (Fig. 2). The hole in the package made by the insertion was sealed with adhesive tape immediately after insertion of the cages. Eight consumer packages were stacked in an acrylic fumigation box (volume: 100 liters; equipped with gas injection and sampling ports, temperature probe, circulation fan, and air-inlet and exhaust valves) and were fumigated with the following fumigation standard. Phosphine was applied in gaseous form using a gastight syringe. Forced aeration was done for one hour after fumigation. The tests were replicated three times.

Fumigation standard: PH₃ 0.82 g/m³ (equivalent to aluminum phosphide [AlP] 2.5 g/m³) for 72 hours at 15°C with 0.16 kg/l load.

1 Estimate at 20 µm thickness.
(e) Evaluation of fumigation efficacy (gas penetration)

Both the confused flour beetle, Tribolium confusum, adults and Indian meal moth, Plodia interpunctella, larvae were stored in a rearing room (25°C, 60% RH) from 4 to 6 days after fumigation, and mortality of the tested insects was determined under a binocular stereo microscope.

(f) Monitoring of gas concentration in the air inside the fumigation box during fumigation

Monitoring of gas concentration in the air inside the fumigation box during phosphine fumigation could contribute to estimating gas penetration into plastic packaging. Gas monitoring was performed with the fumigation conditions (PH$_3$ 0.82 g/m$^3$ for 72 hours at 15°C) described above, and the load for rice packages was increased from 0.16 kg/l to 0.20 kg/l in order to make the difference in concentrations clearer. The intervals of gas measurement were set at 0.5, 1, 2, 3, 6, 24, 48, and 72 hours after injection of phosphine into the fumigation boxes. A 29.5-liter acrylic fumigation box equipped with gas injection and sampling ports, a temperature probe, a circulation fan, and exhaust valves was used. Phosphine gas concentration was determined using a gas chromatograph with FPD (Shimadzu GC-2014).

2. Gas desorption test

(a) Test rice and test plastic package

The test rice and plastic package were the same as those used in the gas penetration test described above, except for the number of ventilation holes in the plastic package. To investigate the influence of ventilation holes more clearly, packages with no ventilation holes and packages with holes added (14 holes per package in total) were fumigated, and gas desorption levels were compared between the two types of package (Fig. 3).
(b) Fumigation and measurement of desorption gas

Each consumer package without holes and those with 14 holes were loaded into the acrylic fumigation box used in item 1(e) and fumigated with the same fumigation schedule described in item 1. After 1 hour aeration using a forced exhaust system, the box door was temporarily opened and gases remaining inside the package were quickly collected by introducing the needle of a gastight syringe directly into the center of the package; the box door was then immediately closed. Gas collections were similarly repeated at 24, 48, and 72 hours from the completion of aeration, and simultaneously gas in the box spaces which should be desorbed from the fumigated package was also collected just before opening the door. The concentrations for all gases collected were also determined using gas chromatography as described above. After the series of gas collections every 24 hours, forced exhaust (5 L/min.) for 5 minutes was done to purge phosphine gas filling the box space for the next gas sampling in order to simulate a commercial shipment of fumigated rice at a warehouse. Holes made by the syringe needle were immediately sealed with plastic adhesive tape after gas collection. The tests were replicated two times.

3. Residue analysis

(a) Test rice and test plastic package

Rice in consumer packages identical to that used in the above gas desorption test was also used to investigate the relationship between desorption and residue. After completing gas collection at 72 hours from the termination of aeration in the above gas desorption test, each type of consumer package was opened, and 90 g of polished rice was placed into gastight vials (volume: 100 ml) as samples. They were then tightly sealed and reserved for 15 days in a refrigerator (5°C) until the day of analysis in order to prevent phosphine emission from the rice.

(b) Analysis

Residue analysis was carried out at the Research Division of the Yokohama Plant Protection Station. The gastight vials were opened just before analysis, and 2 g of rice was transferred into a 20 ml vial for an autosampler with 10 ml distilled water and sealed with a septum and an aluminum cap. Phosphine residue was determined by headspace gas chromatography in the same way as described in MISUMI et al. (2008). The test for verifying sample stability during reservation in the refrigerator was omitted because the object of this residue analysis is to compare residue values of rice between packages with no holes and package with 14 holes. The statistical software JMP 4.0.5J (SAS Institute, Cary, N.C., USA) was used for statistical analysis.

Results and Discussion

1. Gas penetration test

Table 1 shows mortalities of the confused flour beetle (adult) and the Indian meal moth (larva) fumigated with the fumigation standard (PH₃ 0.82 g/m³ [equivalent to AIP 2.5 g/m³] for 72 hours at 15°C).

All of the tested insects in the trials were killed completely by phosphine fumigation. Figure 4 shows the changes in gas concentration in the box space over time during phosphine fumigation. At the initial phase of fumigation, gas con-
Table 1. Mortality of two stored-product insects in rice in consumer packaging fumigated with PH3 0.82 g/m³ for 72 hours at 15°C

<table>
<thead>
<tr>
<th>Species</th>
<th>Stage</th>
<th>Treatment</th>
<th>Number of insects (Alive/Treated)</th>
<th>Mortality (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T. confusum</td>
<td>Adult</td>
<td>PH₃</td>
<td>0/450</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Untreated control</td>
<td>447/450</td>
<td>0.7</td>
</tr>
<tr>
<td>P. interpunctella</td>
<td>Larva</td>
<td>PH₃</td>
<td>0/300</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Untreated control</td>
<td>212/300</td>
<td>29.3</td>
</tr>
</tbody>
</table>

Note: Results were obtained from 3 replications for T. confusum and 2 replications for P. interpunctella.

Fig. 4. Changes in gas concentration in the space inside the fumigation box during phosphine fumigation for rice packages with a load of 0.20 kg/l.

centration was ca. 15–20% higher than the standard’s dosage of 0.82 g/m³, and this higher level continued with a slight gradual increase until the 3-hour measurement point. Gas concentration at the 6-hour measurement point, however, had decreased sharply from 1.0 mg/l to 0.97 mg/l. After this point, gas concentrations did not fluctuate and slowly decreased to 0.92 mg/l. It is considered that the most phosphine gas may penetrate into plastic packaging between the 3-hour and 6-hour measurement points, and then it affected the test insects.

Sheeted bag-stack fumigations of paddy rice using AIP showed that sorption appeared to be a major limiting factor, reducing the potential fumigant dosage by about 50% (WANG et al., 2006). In our study, gas concentration is maintained higher than the initial dosage (PH₃ 0.82 g/m³) for the whole duration of fumigation. Therefore, to fumigate polished rice without chaff was expected to maintain proper gas concentration compared with the fumigation of paddy rice. Polyethylene film has been used in PH₃ fumigation under tarpaulins for the purpose of maintaining gas retention as the film covers stacked bags (COGBURN, 1974; THIEM et al., 1974; RAJENDRAN and MURALIDHARAN, 2001). Accordingly, film thickness and other factors properly affect phosphine penetration into packaging. However, an amount of phosphine gas that could completely kill test insects should penetrate into the center of consumer packaging through polyethylene film if some ventilation holes are present on it. Although it is difficult to estimate what amount of phosphine could penetrate into packaging, the amount of gas that can penetrate into packaging should also depend on the concentration in the air spaces in the fumigation box. Warehouses possessing high levels of gas tightness should be better for commercial phosphine fumigation at export; alternately, to investigate accurate penetration rates into consumer packaging, it is necessary to secure appropriate fumigation.

2. Gas desorption test

Generally, in commercial-scale quarantine fumigation, aeration is carried out for a certain number of hours after completing scheduled fumigation in order to lower gas concentrations to safe levels as prescribed in regulations. The speed of gas desorption from consumer packaging through plastic film must be affected by aeration periods, which in turn may influence phosphine residue on fumigated rice and the safety of workers who execute either fumigation or shipment. Table 2 presents both gas concentrations in the space inside the fumigation box and the gas remaining in
Table 2. Phosphine gas concentration measured in chamber space or inside consumer packages fumigated with PH$_3$ 0.82 g/m$^3$ for 72 hours at 15°C

<table>
<thead>
<tr>
<th>Consumer package</th>
<th>Location of gas sampling</th>
<th>During fumigation</th>
<th>Time after termination of forced aeration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>60min. (mg/l)</td>
<td>72hr (mg/l)</td>
</tr>
<tr>
<td>Ventilation hole × 0</td>
<td>R1 Chamber space</td>
<td>0.99</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>R2 Chamber space</td>
<td>0.95</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>Inside package</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ventilation hole × 14</td>
<td>R1 Chamber space</td>
<td>0.95</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>R2 Chamber space</td>
<td>0.94</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>Inside package</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: “R1” and “R2” mean Replication 1 and Replication 2, respectively.

plastic packaging in two replication studies. Gas concentrations during fumigation did not show a particular difference whether ventilation holes were present or not.

Desorption into the box space from packaging: Focusing on concentrations in the space inside the fumigation box, 15 ppm was detected for the package without ventilation holes at the 24-hour measurement point, but a slight higher value of 17 ppm was detected in the case of the package with 14 ventilation holes. Concentrations of 4–5 ppm and 1 ppm for the package without holes were confirmed at the 48-hour and 72-hour measurement points, respectively. On the contrary, for the package with 14 holes, both measurement points provided values less than the quantitative limit (<1 ppm).

Gas remaining inside packaging: Gas concentrations inside packages without holes remained continuously higher than others over time. The results showed that higher concentrations, from 519 ppm at 10 minutes through 59 ppm at 72 hours, still remained in spite of the 1-hour forced exhaust that was done after fumigation. Concentration inside the package with 14 holes, detected at 312 ppm at the 10-minute point, rapidly decreased to ca. 20 ppm at the 24-hour point, and after the 48-hour point all values were indicated below 1 ppm.

Based on the desorption test and oxygen permeability rate of polyethylene film, an amount of phosphine gas can permeate packaging film and could penetrate inside the package; it can also desorb out of the package regardless of ventilation holes. However, the number of ventilation holes certainly affects smooth phosphine desorption from consumer packaging. Gases inside packages with 14 holes speedily decreased, whereas desorption from packages without holes was obviously delayed. A 5-minute forced aeration every 24 hours was performed to simulate as closely as possible actual shipping of rice in warehouses. Desorbed gas acquired at the 48-hour point still indicated 4–5 ppm, beyond the threshold limit of 0.3 ppm for worker safety set in the regulations (MAFF, 1968; MoL, 1972). It is reported that polyvinyl chloride (PVC) sheeting showed higher phosphine retention than polyethylene in tests under environmental conditions (VALENTINI et al., 1997). Taking into account the material of films, sufficient aeration time using a forced exhaust unit is the most important measure for safety after fumigation of polished rice in plastic packaging for commercial fumigation. The aeration time should be longer than that of other usual fumigation procedures in the quarantine system.

3. Residue analysis

The results of phosphine residue analysis are provided in Table 3.

According to Table 2, gas concentrations that remained inside packages without holes at the 72-hour point after termination of aeration were 62 and 59 ppm for replication 1 and 2, respectively. The concentrations for packages with 14 holes were less than 1 ppm, which means the concentrations of gas remaining inside the packages differed by almost 60 times between the two types of package. Therefore, large residue levels were expected in the analysis for packages without holes, and actual levels of residue in the packages without holes were from 0.0011 to 0.0014 ppm, not indicated as much higher values compared to residues acquired in analysis of the packages with 14 holes, which were from 0.0009 to 0.0011 ppm. The difference between them was detected at only 1.5 times, although significant differences were ob-
Table 3. Phosphine residue for rice in consumer packaging fumigated with \( \text{PH}_3 \) 0.82 g/m\(^3\) for 72 hours at 15°C

<table>
<thead>
<tr>
<th>Type of package</th>
<th>Replications</th>
<th>Residual rate-1 (ppm)</th>
<th>Residual rate-2 (ppm)</th>
<th>Mean residual rate(^1) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ventilation hole × 0</td>
<td>1</td>
<td>0.0014</td>
<td>0.0012</td>
<td>0.0013</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0011</td>
<td>0.0012</td>
<td>0.0011</td>
</tr>
<tr>
<td>Ventilation hole × 14</td>
<td>1</td>
<td>0.0011</td>
<td>0.0011</td>
<td>0.0011</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0009</td>
<td>0.0010</td>
<td>0.0009</td>
</tr>
</tbody>
</table>

Notes: \(^1\)There are significant differences between ventilation hole × 0 and ventilation hole × 14 (Median test, \( a = 0.05 \)). The add and correction rates for phosphine on 3 replications were 109%, 107%, and 110%, respectively. Analysis was conducted after 15 days reservation in a refrigerator at 5°C.

served in residues between the package without holes and the one with 14 holes (Median test, \( a = 0.05 \)).

MOLINARI et al. (1993) investigated phosphine residues for varieties of wheat in sacks fumigated with 1 or 2 g/m\(^3\) phosphine. It showed a mean level of residue of 1.4, 0.5, and 0.6 \( \mu \)g/kg from 48 to 72 hours after fumigation. Regardless of different packaging and commodities, phosphine residues of a similar level were obtained in each investigation. Consequently, it is considered that phosphine residues on fumigated rice were not mainly dependent on the remaining gas concentration inside packaging after fumigation, and estimating residue levels based on the values of such concentration data seems to be difficult. Regardless of packaging or ventilation holes, all residue values determined in this study were indicated at a much lower level than maximum residue limits (MRLs), which are set at 0.1 ppm for rice in Japan (MHW, 1959). Exceeding MRLs in rice fumigated with the phosphine fumigation standard may be unlikely even if polyethylene film is used as packaging for polished rice in commercial fumigation in Japan.

Acknowledgements

We would like to thank Mr. Hiroaki KATO and Mr. Ken MASUDA of the JA Pearl Rice Eastern Japan Corp. for providing valuable information on the distribution system of Japanese rice.

REFERENCES


和文摘要

米の販売用容器包装がリン化水素ガスの浸透性・脱着性及び作物残留に与える影響

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ポリエチレン製米袋に入れられた精米に対してリン化水素くん蒸を実施し、その袋内へのガス浸透、袋からのガスの脱着及びくん蒸された精米への残留値に対する袋フィルムの影響について調査した。2kg詰めパッケージの中心部に挿入されたヒタタコクノストモドキ成虫とノシメマグラメイガ幼虫は、リン化水素0.82g/m³、72時間、15℃のくん蒸において完全殺虫され、ポリエチレンフィルムを通じても供試虫を十分殺虫できる濃度のガスが浸透できたことが判明した。脱着については、通気孔が無い袋内のガス濃度は、通気孔が14ヵ所のある袋に比較して高い濃度であった。通気孔が無い袋内のガス濃度は、くん蒸後1時間の排気終了前から起算して10分後で519ppmから72時間後の59ppmであり、これに対し、通気孔14ヵ所の袋において袋内のガス濃度は、くん蒸後24時間後に急速に20ppmまで減少し、48時間後においては、全てガス濃度は1ppm以下となった。これにより、通気孔の数が多ければ袋からのリン化水素ガスの脱着に影響していると考えられる。なお、脱着の試験に使用したものと同一のパッケージについて、ヘッドスペースガスクロマトグラフ法による米のリン化水素の残留分析を実施した結果、通気孔無しの場合の残留値は0.0011～0.0014ppmであり、通気孔有りの場合の0.0009～0.0011ppmと比較してそれほど大きくなく、通気孔の有無は残留値を左右する主要な要因ではないと考えられた。なお、通気孔の有無には関係なく、得られた残留値はすべて日本の残留基準値の0.1ppmを大幅に下回っていたが、作業者の安全性確保の観点からは、ガス脱着を促進するため、通常より長い排気時間が必要であると考えられた。

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