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MEASUREMENT OF DELAYED EVOLUTION OF PHOSPHINE FROM SOLID FORMULATION THROUGH PLASTIC PACKAGING

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ABSTRACT

To further investigate the technique used in China of retarding phosphine evolution from solid aluminium phosphide formulations by enclosing the tablets in plastic bags placed inside the fumigation enclosure, we monitored phosphine production under laboratory controlled conditions. An apparatus comprising a computer-controlled sampling manifold and an electrochemical sensor was used to continually determine and log phosphine concentrations. Commercial 3% phosphide tablets were placed in glass dishes that were then covered with plastic of known water permeability and sealed inside chambers where they were exposed to gentle streams of humidified air (70% r.h.). A computer controlled the monitoring of the PH₃ concentrations of the effluents, so that the attenuation in PH₃ production with respect to uncovered tablets was determined. The effect of plastic thickness on PH₃ evolution was examined, where it was found that even very thin plastic (10 µm) drastically reduced the rate of PH₃ evolution. The rate of production of the gas was only partially dependent on the number of tablets within the enclosed dishes. Lastly, the surface area of the permeable plastic was shown to affect the rate at which PH₃ was produced.

We discuss the utility of the “delayed evolution” technique in relation to the need to prolong exposure periods for effective PH₃ fumigations.

INTRODUCTION

Phosphine (PH₃) has been used to protect stored grains and oilseeds in the Peoples Republic of China since 1963 (Tan Xianchang, 1998). To improve the efficacy of this fumigant, and reduce the dosage applied, a number of techniques have been developed in China that extend exposure periods. These include; intermittent fumigation (Fan Jing Chen, 1990), the ‘double low’ (low oxygen, low PH₃ dosage), and ‘triple low’ (low temperature, low oxygen, and low PH₃ dosage) fumigation/storage techniques.

To extend the time over which PH₃ is evolved a slow release technique was developed whereby aluminium phosphide tablets (or pellets) are enclosed in polyethylene bags that are closed using string, by knotting the top of the bag or by heat sealing then placed inside the fumigation enclosures (Fig. 1). This has the effect

of retarding moisture ingress to the aluminium phosphide thereby slowing down production of PH_3 (Cao *et al.*, 1983; Tan, 1998).



Fig. 1. A bag stack being fumigated with phosphide tablets in plastic bags. Guangzhou, China, October 1998.

This technique, and its development, was recorded in the Chinese literature (Anon., 1985) but was not widely known outside China. It is widely used to ensure that polished rice is stored safely through summer by inhibiting moulding (Li *et al.*, 1983; Ren, Pers. comm.). It has also been used in China to control mites (Ruan *et al.*, 1993; 1999), for which double or extended exposure periods are required (Anon., 1998). Depending upon the thickness of polyethylene membrane used, it can take 90 days, or more, for the aluminium phosphide formulation to become fully spent (Ren, Pers. comm.). In situations where a more rapid (yet still delayed) evolution of PH_3 is required, holes are pricked through the bags with needles (Ruan *et al.*, 1993). Another method used to prolong exposure to PH_3 is the “split method.” Half the tablets are placed inside the stack at the start of the fumigation and the rest are added a week later (Cao *et al.*, 1999).

Extended exposure periods are also required to control strains of stored-product insects resistant to PH_3 (Chaudhry, 2000). It has been suggested that aluminium phosphide, specially formulated for slow release of PH_3 , may provide a means for ensuring that a sufficient level of PH_3 can be maintained for a long enough period to produce an effective dose (Rajendran, 2000). While this approach might prove to be successful, the economics of manufacturing special slow release formulations of aluminium phosphide preparations have yet to be established by manufacturers. Thus it has been suggested that the slow release technology using polyethylene films described above might provide a simpler, more immediate, and economic response

to the need to extend exposure periods in situations where the gas may be rapidly lost, such as when fumigations of bag stacks under gas proof sheets are undertaken (Rajendran, 2000).

Banks (1987) developed an analytical method for continuous laboratory measurement of PH_3 production by AIP formulations. He then used it to examine the factors affecting the rate of PH_3 production (Banks, 1991). He found that the “shape of the cumulative release curve was unaffected by gas flow rate over the formulation or by temperature, humidity or manufacturer”. He also found that the absolute water content of the gas, not the temperature or r.h., determined PH_3 release rates. Ducom and Bourges (1993) performed simplified analyses of phosphine formulations.

This paper reports on a preliminary laboratory investigation to examine the feasibility of prolonging exposure periods in disinfestation treatments undertaken with PH_3 in situations where the gas may be lost rapidly from the fumigation enclosure.

MATERIALS AND METHODS

Aluminium phosphide preparations were exposed to a stream of humidified air passing through desiccators. Concentrations of PH_3 released by the preparations into the effluent air stream were monitored to determine rate of PH_3 production using the apparatus described below.

Apparatus

A schematic diagram of the apparatus, set up inside a fume hood, is shown in Fig. □. Dry filtered compressed air, metered through a Mass Flow Controller (Brooks 5850 - MFC) to ensure a steady flow, was humidified to 70% r.h. by passing it through two humidifiers fitted with glass frits linked in series. The humidifiers contained a distilled water/glycerol mixture (specific gravity 1.165 - 1.170). The water content of the water/glycerol mixture was topped up twice per day. The humidified air was passed through a plenum chamber (a three-necked round bottom flask) containing an electronic temperature sensor (LM 35) and an electronic humidity sensor (Vaisala Humitter).

The air was then divided into six streams through a 1-to-6 manifold controlled by six Brooks flow meters and led through six exposure chambers (2.5 L desiccators fitted with dreschler heads). The effluent airstreams passed through a bank of six two port solenoid valves through a 7-to-1 manifold to the PH_3 sensor (see below) and then to atmosphere. The seventh inlet of the manifold was connected to a continuous flow of nitrogen humidified to 50% r.h. using a distilled water/glycerol mixture (specific gravity 1.165-1.170), that flushed PH_3 from the system and sensor between readings.

The flow rates through the chambers were sensitive to inter-chamber variations of tube length and constriction by fittings, and changing one flow rate affected the others, so the flowmeters were used to indicate that the system had not developed

leaks or blockages. A digital flowmeter was periodically used to accurately record the flow through each chamber. It was assumed that since the flow rates were so small (*ca.* 100 mL min^{-1}) compared to the size of the chambers (*ca.* 2,500 mL), that flow rate would not influence PH_3 production.

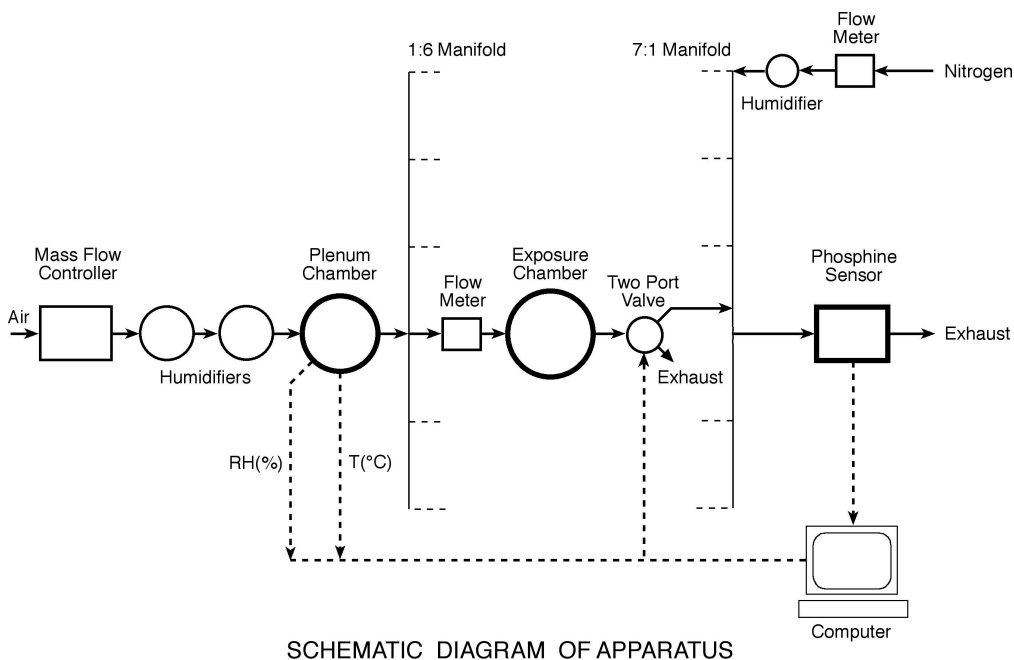


Fig. 2. Schematic diagram of laboratory apparatus used to expose aluminium phosphide formulations to humidified air, and record the evolution of phosphine from them. Air (at left of diagram) was humidified and passed into a plenum chamber where its r.h. and temperature were recorded. It then passed into a 6-way manifold. Each branch (one shown in detail) was metered before it passed into an exposure chamber, where the aluminium phosphide tablet was placed. The effluent then normally passed to the exhaust. The computer switched the valves one at a time, so that the effluent (diluted by nitrogen) passed over the PH_3 sensor. The computer made one reading each ten minutes, so that the chamber effluents were measured once per hour.

Data acquisition and processing

A computer, running Windows 95 and a “strategy” (computer program) written by the authors in Advantech Genie (v.3.04) was fitted with an Advantech PCL-18L data acquisition and control (DAC) card. This controlled a bank of six 3-way solenoid valves, which were connected to the outlets of the 6 chambers. The valves were plumbed so that effluent streams were normally vented to atmosphere inside the fume hood, and passed them into a 7-to-1 manifold only when the valves were energised. The outlet of the manifold led to an electrochemical PH_3 sensor (Canary

Co.). The seventh inlet to the manifold was connected to a continuous stream of nitrogen, humidified to approx. 50% r.h., which flushed PH₃ from the system and sensor between readings. The PH₃ sensor was a 4-20 mA transmitter driving its signal across a calibrated 250 Ω resistor on the DAC card.

The strategy operated at timescales of ten minutes (for chamber switching and data logging) and one second (for measurement of PH₃, temperature and r.h.). After the PH₃ sensor's signal had stabilised (usually about 120 sec) the data (timestamp, chamber number, PH₃ concentration, temperature and r.h.) were recorded and the valve closed, so that the sensor was not exposed to PH₃ more than was necessary. The sensor was calibrated by comparing its output (in volts) to GC/FPD determinations of effluent airstreams.

Calculation of production rate

At the end of an experiment, the log file was processed using a spreadsheet program. Timestamps were converted to elapsed times and sensor voltages were converted to PH₃ concentrations. Allowances were made for PH₃ dilution by the make-up nitrogen. In Eq. 1, where C is PH₃ concentration, in parts per million (v/v) (ppm), V is the voltage reading of the sensor and f_{ch} & f_{dil} are the flowrates through the exposure chamber and of the diluent nitrogen, respectively. The scaling coefficient, k (ppmV⁻¹) was determined from the calibration curve (see Results).

$$C = kV \frac{f_{ch} + f_{dil}}{f_{ch}} \quad (1)$$

Phosphine concentrations (in ppm) were converted to concentrations (in mg L⁻¹) by applying the approximation 1 mg L⁻¹ = 745 ppm (at Canberra's mean air pressure of 735 mmHg). They were then converted to PH₃ production rates, R (mg h⁻¹) as shown in Eq. 2.

$$R = Cf_{ch} \quad (2)$$

Experiments

Initially, the exposure chambers were loaded with bare aluminium phosphide tablets (QuickPhos, United Phosphorus, Mumbai, India), to ensure that PH₃ concentrations in the effluent airstream remained on-scale, and to test the apparatus. Tablets were removed from their storage container immediately before use and the container was flushed with dry nitrogen before resealing.

One or more tablets were placed in a dish (generally a glass crystallising dish, diameter 75 mm; height 44 mm). It was covered with plastic film and sealed with rubber bands. The dishes were then placed in the chambers, which were sealed and connected to the apparatus as quickly as possible. The process of loading the chambers took no more than 10 minutes. Treatments were conducted in duplicate. Spent and partially-spent tablets were allowed to react with airborne humidity in a

large beaker at the rear of the fume hood for several days, then the residue was soaked in water and detergent overnight and disposed of.

Experiment 1: The effect of plastic film thickness was examined by placing tablets in identical crystallising dishes. One pair was left uncovered, and the other two pairs were covered with polyethylene film of known thickness (30 mm and 50 mm).

Experiment 2: The contribution of the quantity of aluminium phosphide to the rate of production of PH_3 was examined by placing 1, 2 or 4 tablets into pairs of dishes, then covering them all with the same plastic film (commercial food-grade cling wrap, 10 μm thickness).

Experiment 3: The effect of surface area (SA) of plastic film was investigated by replacing four of the crystallising dishes (SA 4418 mm^2) with pairs of smaller dishes (SA 1735 mm^2) and vials (SA 452 mm^2). A single tablet was placed in each dish, which were then covered with cling wrap.

RESULTS

The PH_3 sensor's response was linear and conformed to equation (3), where $C = \text{PH}_3$ concentration in ppm and $V = \text{volts}$. $R^2 = 0.895$.

$$C = 260V + 7 \quad (3)$$

A representative graph of raw data obtained from a logfile of a single chamber is shown in Fig. 3. The r.h. and temperature remained fairly steady during the 4 days of the experiment, and the recorded PH_3 levels from the chamber followed the expected pattern, of rapid onset, after addition of the tablet at $t=14$ h, and gradual decline of production until levels were immeasurably small. The PH_3 sensor remained within its scale of 1 V (at zero reading) to 5 V (at full scale).

Throughout the experiments, flow rates through each chamber remained relatively constant. However, the rates from chamber to chamber ranged from 60 to 150 $\text{mL}\cdot\text{min}^{-1}$. This implied nominal "complete air change" times of 20 to 40 minutes, which was less than the hourly interval at which the PH_3 concentration in the effluent was measured. To test how well the chambers were flushed, injections of 10-40 mL of source PH_3 were made into the inlets of the chambers. The PH_3 readings fell to near-zero within 1-2 h following these injections.

The placement of plastic film greatly retarded the rate of PH_3 evolution (Figure 4). In the graph, the rates are shown on a logarithmic axis so that the differences between the two thicknesses of film can be seen in relation to the uncovered tablets. The tablets under the thinner film evolved PH_3 faster than those under the thicker film, but they were both about 100 times slower than the uncovered tablets' evolution rate.

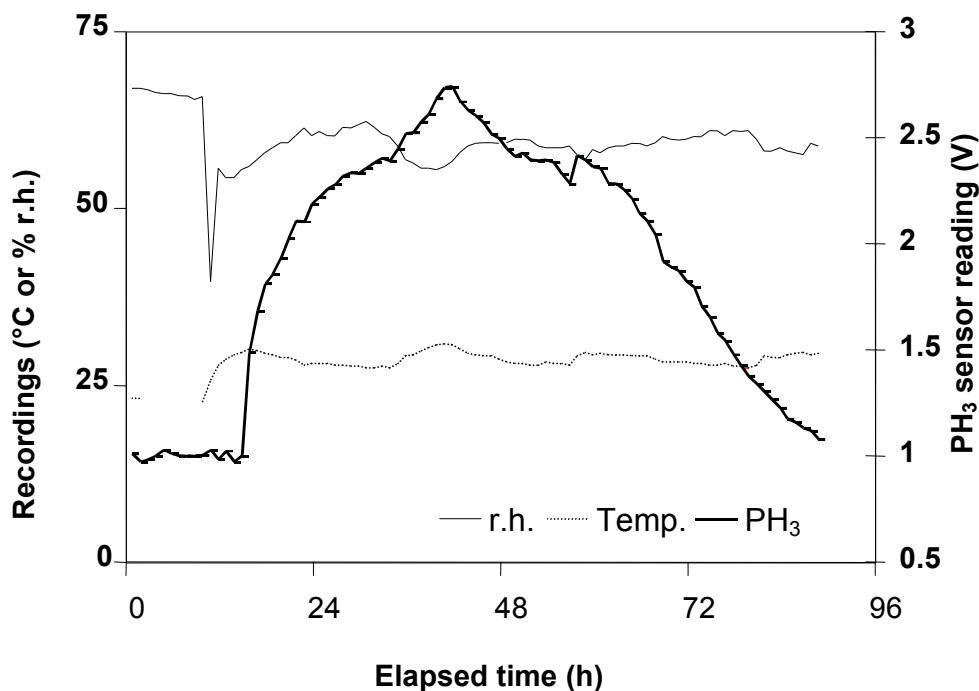


Fig. 3. Raw data obtained from log file, for a single exposure chamber (bare tablet). The phosphine sensor readings are plotted against the right hand axis, and the temperature and r.h. are plotted against the left hand axis.

In view of the slow rate of evolution under the thicker plastic films, experiment 2 employed commercial clingwrap so as to increase overall evolution rates. Dishes containing 2 or 4 tablets produced PH_3 at much the same rate, i.e. approx. $8 \mu\text{gmm}^{-1}$, and those containing 1 tablet at a slightly lower rate ($7 \mu\text{gmm}^{-1}$), as illustrated in Fig. 5. Exposure began at $t=3$ h. During the experiment, it was observed that the readings from some of the chambers had unexpectedly begun to rise. Close examination of the plastic films within the chambers showed that a large hole had appeared in the plastic covering chamber 1a and a smaller one had formed in chamber 2b, both after approximately 15 h.

The investigation of the effect of surface area on evolution rate showed that the rate of evolution per unit area was approximately $1 \mu\text{gmm}^{-1}\text{mm}^{-2}$ (Fig. 6). The apparatus failed in one of the '1735 mm^2 ' chambers, so this treatment was represented by single readings alone.

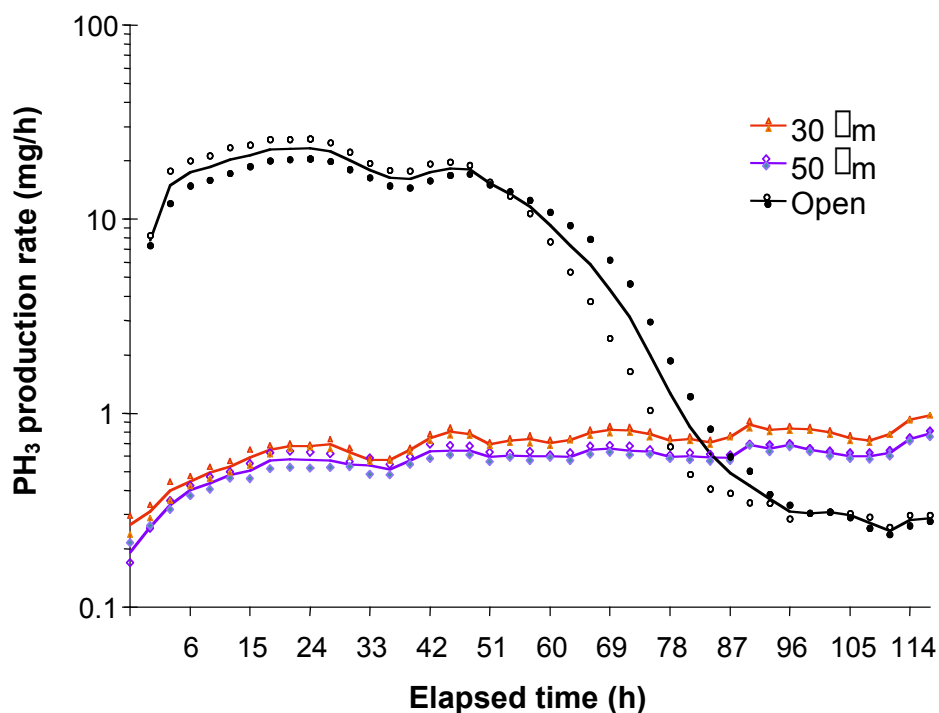


Fig. 4. Effect of plastic film thickness on PH_3 production rate. A logarithmic scale is used on the y axis to show clearly the data, which vary over two orders of magnitude.

DISCUSSION

The rate of PH_3 evolution was dependent on the thickness of the plastic (Fig. 4) and its surface area (Fig. 6). The placement of more than one tablet in the dishes had only a small effect on the PH_3 production rate (Fig. 5) and this may indicate that other factors than water diffusion were partially limiting at this ratio of film surface area to aluminium phosphide. In practice, the amount of formulation is generally large with respect to the size of the plastic bag (Fig. 2). Overall, this supports the hypothesis that the chief limiting factor was the penetration of water vapour through the plastic.

It is not known how permeable the plastic films were to PH_3 , but this is not important for two reasons. Firstly, it is already known that PH_3 readily absorbs into and penetrates most plastics (Waterford and Winks, 1986). Secondly, the high concentration gradient that would be formed if the plastic were not freely permeable to PH_3 would ensure that a steady state (where the rate of escape of PH_3 from the

enclosed dish was balanced by the rate of formation of the gas from the tablet) would rapidly come into existence.

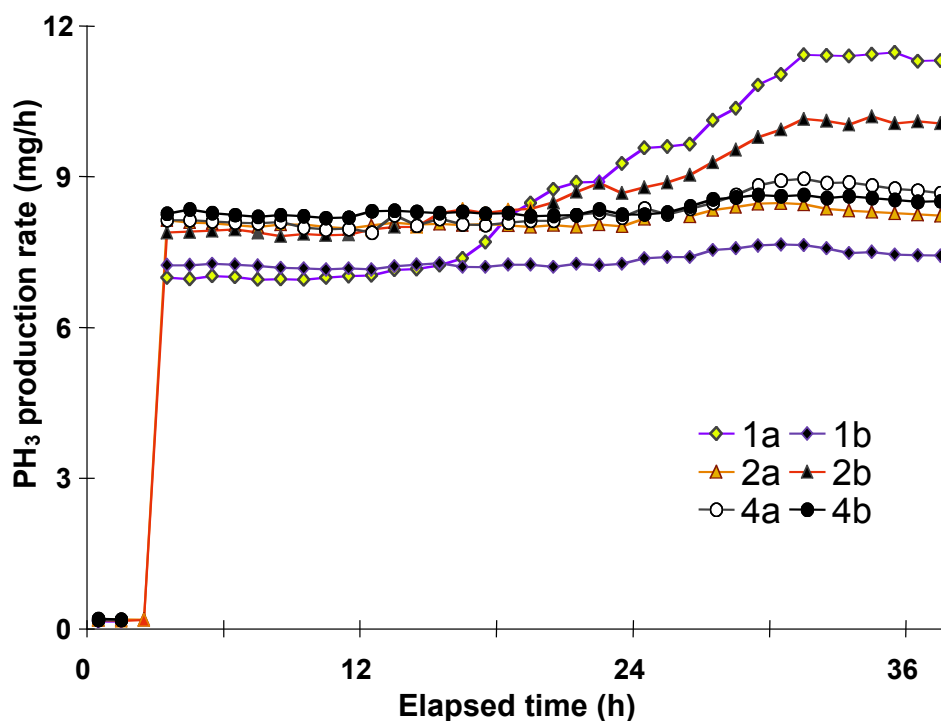


Fig. 5. Effect of number of tablets in a dish. Six identical dishes were charged with 1, 2 or 4 tablets and immediately covered with domestic clingwrap film. The sudden rise in readings when the chambers were loaded (at $t=3$ h) indicates that PH_3 production commenced immediately. There was a small increase in PH_3 production between the 1 tablet and 2 tablet treatments, but it was a lot less than 100%. In some cases, rips developed in the film, and output rates rose (1a and 2b).

No attempt was made to correct the data in the graphs for occasional fluctuations in temperature, and hence water content of the airstream, that occurred in the laboratory. The relative production rates between treatments were unaffected by these changes. Previous work has shown that reaction rate is a function of absolute water vapour concentration, not relative humidity or temperature (Banks, 1991). A humidification system that was not sensitive to temperature fluctuations would be expected to produce smaller or no fluctuations of this sort.

The flow rates were set so as to mimic the relatively static conditions, which would prevail inside a bag stack. There was some variation in flow rate between the chambers, but after application of the appropriate flows in Eqs. 1 and 2, the

agreement between the calculated production rates of the replicates was very much smaller than the differences in flow rates between the chambers. This indicates that the small variations in the flow rates (above a certain limiting flow) did not affect the production rate. The marked slowing of PH_3 production in our treatments did not allow the complete reaction of the phosphide tablets, even when the exposure period was more than a week (see Fig. 6). It can only be assumed that the total amount of PH_3 produced would have been the same as for uncovered tablets.

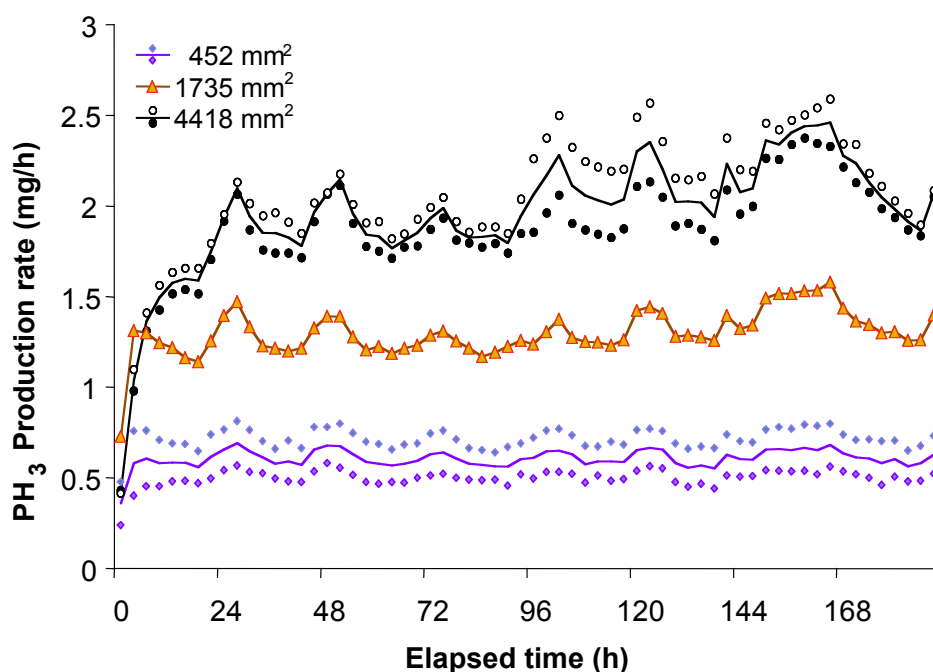


Fig. 6. Effect of surface area of plastic film on PH_3 production rate. The PH_3 production rate was dependent on the surface area of the plastic film. Single tablets were placed in vials or dishes with surface areas of 4418, 1735, and 452 mm^2 . The points indicate individual replicate readings, and the solid lines are the average production rates for each treatment. Note: The apparatus failed in one of the “1735 mm^2 ” chambers, so this treatment is represented by single readings alone.

The occurrence of small rips in the stretched clingwrap (Fig. 5) after some period of exposure to PH_3 is intriguing. It is possible that the gas weakened the plastic by reacting with residual alkene oligomers, which may be present in the polyethylene. It was noted that the tears always occurs along the ‘grain’ of the plastic.

On the basis of our observations, we suggest that the method of slowing the production of PH_3 from aluminium phosphide tablets or pellets merits further attention. A variation on the “Chinese” method of hanging tablets inside small

grocery bags may be to cover rigid plastic “lunchboxes” with a plastic film. This would allow better control over PH_3 evolution rate, and presumably make collection and disposal of spent residues easier. Fumigation by delayed evolution may be an important means of combating the spread of PH_3 resistance in circumstances which dictate a method, which requires cheap materials and simple application, and the sealing of fumigation enclosures is not practicable. We note that the lengthening of exposure periods may go against the economic imperatives to quickly complete a treatment, that are often placed upon fumigators.

Similar trials at a larger scale (50 t bins) are planned.

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