

AN INVESTIGATION INTO SAFE DISPOSAL OF PHOSPHINE-GENERATING FORMULATIONS

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ABSTRACT

Recommended methods for disposal of phosphine (PH₃) formulations require immersion, combustion or burial. All can pose safety hazards to workers. Although burial has been recommended, no clear operating procedures have been defined.

This investigation examined the efficacy and occupational safety of the burial of PH₃-generating formulations. Partially spent and unspent blankets, pellets and tablets were buried in soil at two depths. PH₃ levels generated by the buried formulations were monitored both within and immediately above the burial site. Above the burial site, PH₃ levels fell below the 0.3 ppm Threshold Limit Value (TLV) within 25 d.

INTRODUCTION

Aluminium phosphide (AIP) formulations are used to produce phosphine (PH₃) gas for fumigation of stored products. The AIP reacts with water vapour in the air to generate PH₃ gas, leaving a residue of aluminium hydroxide (Al(OH)₃) powder. If, for any reason, the fumigation is interrupted before the reaction of the AIP is complete, fumigators are faced with occupational health and safety problems in disposing of the partially spent formulation. Even when AIP is apparently fully reacted (or spent), care is required when disposing of the residue (AFHB/ACIAR, 1994; Friendship, 1989). Several authors have noted that up to 5% of the AIP can remain as unreacted material occluded in fully spent Al(OH)₃ residue (Banks, 1991; Rosebrook, 1972; Winks, 1970).

Disposal directions are usually given by manufacturers, either on the label or in product manuals (Anon., undated; Anon., 1988). However the instructions vary considerably with

respect to both content and detail. The methods fall into two categories: dry methods involve either burial or incineration and wet methods deactivate the AIP or $\text{Al}(\text{OH})_3$ with a detergent in water mixture.

In general, disposal of an unspent AIP formulation requires that it be allowed to stand in the open (protected from the rain) until the material is inactive and then treated with detergent in water and/or buried. Unfortunately, there are no guidelines indicating either when the formulation can be safely treated with detergent in water or the relative quantities that can be safely handled and treated. More importantly, it is neither safe nor practical to allow a formulation to generate PH_3 in the open without taking appropriate precautions concerning worker safety and environmental protection.

A range of AIP PH_3 -generating formulations from several manufacturers had been accumulating at the Stored Grain Research Laboratory since the mid 1970's. The need to dispose of this material presented an opportunity to test burial as a method of disposal. Burial of spent residues is one normally accepted method of disposal, and it was considered that, provided certain conditions are followed, this method should provide a worker-safe and environmentally responsible method for disposal of unspent formulations. In this test unspent AIP was specifically included in order to obtain maximum PH_3 levels and observe their decay to safe levels.

MATERIALS AND METHODS

This investigation was undertaken in New South Wales at the GrainCorp, Parkes sub terminal. A secure location was selected within a bunker site (33° , 10 min, 53 sec S; 148° , 12 min, 54 sec E), where two rows of 15 holes approximately 1 m apart were dug using a mechanical posthole digger fitted with a 300 mm diameter auger. One row of holes was dug to a depth of 500 mm, the other to 250 mm.

The following formulations were placed into these holes: blankets (either rolled up as they were packed in their containers or unrolled), pellets or tablets (Table 1). The formulations were covered with approximately 50 mm soil; then a bottomless 460-ml chamber connected to the surface by a nylon tube (3 mm i.d.) was placed on the soil, providing an airspace from which PH_3 generated by the formulations could be sampled. The chambers were constructed from plastic bottles perforated by six holes (approximately 4 mm diameter), four at the sides and two at the top (Fig. 1). The space around and above the chambers was then filled with soil excavated from the hole, and excess soil was heaped over the hole at ground level. The soil replaced was not tamped down or compacted in any way. Controls, in which no AIP formulations had been buried, were prepared in the same manner.

Underground PH_3 levels, generated by the reaction of the buried AIP formulations, were monitored by sampling gas concentrations through the nylon tubing attached to holes at the tops of the chambers. PH_3 levels were also monitored at two locations (Fig. 2): immediately above the burial site at ground level (at 14 points between the two "columns" of holes and midway between the 15 rows of holes) and above ground level (at

TABLE 1
Depth and contents of two rows of holes on a 2 × 15 m grid

Hole number	Row F (0.5 m)	Row B (0.25 m)
1	Celphos blanket	Control
2	Quickphos blanket	Partially spent pellets
3	6 × 100 g Quickphos tablets	Partially spent tablets
4	2 × 1667 Celphide pellets	Mixed pellets
5	Celphos blanket	Quickphos tablets
6	6 × small Quickphos blankets	Celphos blanket
7	5 × 100 g Quickphos tablets	Small blankets
8	2 × 1667 Phostoxin pellets	4 × 100 g Quickphos
9	Celphos blanket	Celphide pellets approx. 2 flasks
10	Quickphos blanket	Quickphos blanket
11	Mixed pellets approx 2 flasks	6 × small Quickphos blankets
12	5 × small Quickphos tablets	Pellets
13	Partially spent blanket	Pellets
14	Partially spent blanket	Quickphos blanket
15	Control	Celphos blanket

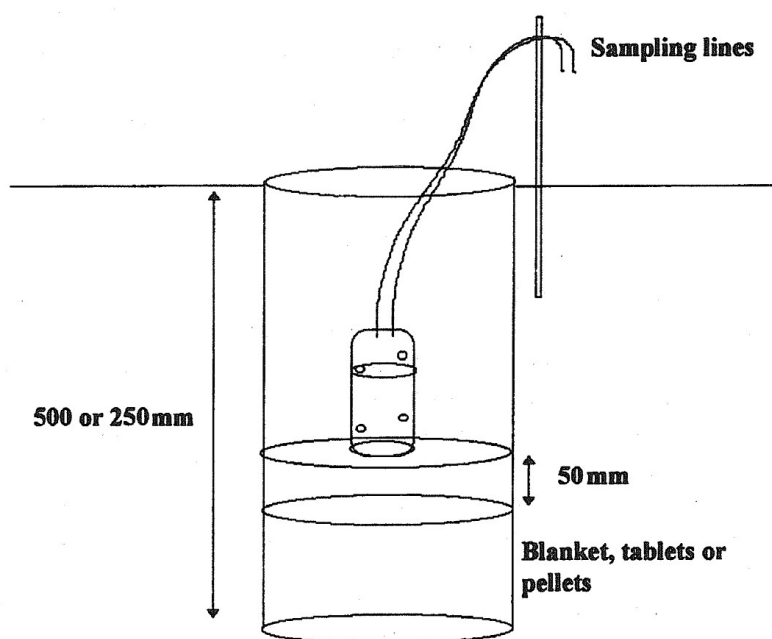


Fig. 1. Scheme of disposal hole and sampling layout.

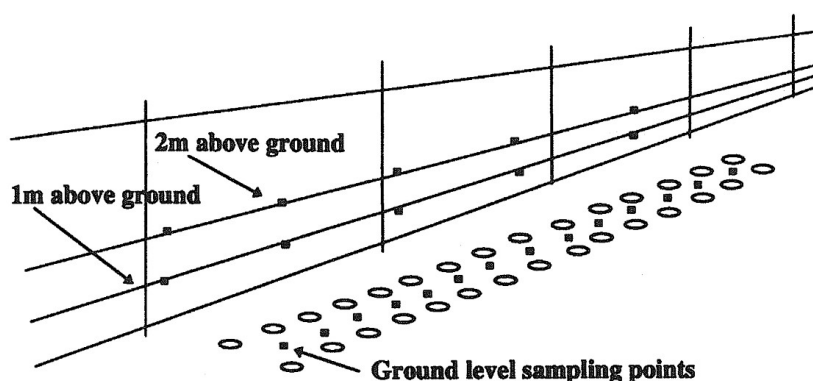


Fig. 2. Schematic of above ground sampling positions relative to disposal holes.

heights of 1 and 2 m along the border of the site in a position generally downwind and 1–2 m from the burial site).

PH_3 levels inside the disposal holes were determined using a calibrated gas analyser (BEDFONTTM Phosphine Monitor, fitted with a CITICEL[®] electrochemical sensor). Each chamber was sampled until a maximum reading was obtained. The instrument was allowed to return to zero before the next sample was measured. Above-ground sampling was carried out with a workspace monitor (Amahsco GEM) also fitted with a CITICEL[®] electrochemical sensor. Both instruments were calibrated against reference standards.

Samples of the soil in which the AIP formulations were buried were taken for classification.

RESULTS

The mean ($n = 14$) ground level PH_3 concentrations (measured at different times after the AIP formulations were buried), compared with mean readings taken at 1 m ($n = 5$) and 2 m ($n = 5$) above ground, are shown in Fig. 3. Windspeed on the day of measurement and total rainfall over the 3 d preceding measurement are also shown.

The mean ($n = 14$) below-ground PH_3 levels measured in the chambers at various times after burial are shown in Fig. 4, with the data for the formulations buried at 500 and 250 mm shown separately. The upper limit of detection in the Bedfont detector used for the measurements in this work was 2,000 ppm, so concentrations above this value could not be quantified.

For the first 2 weeks after burial, high ($>2,000$ ppm) concentrations of PH_3 were observed in the control holes, indicating that PH_3 can diffuse laterally at least 1 m through the soil. For this reason, comparisons between the different formulations are not possible, and samples will need to be buried much farther apart in any future work.

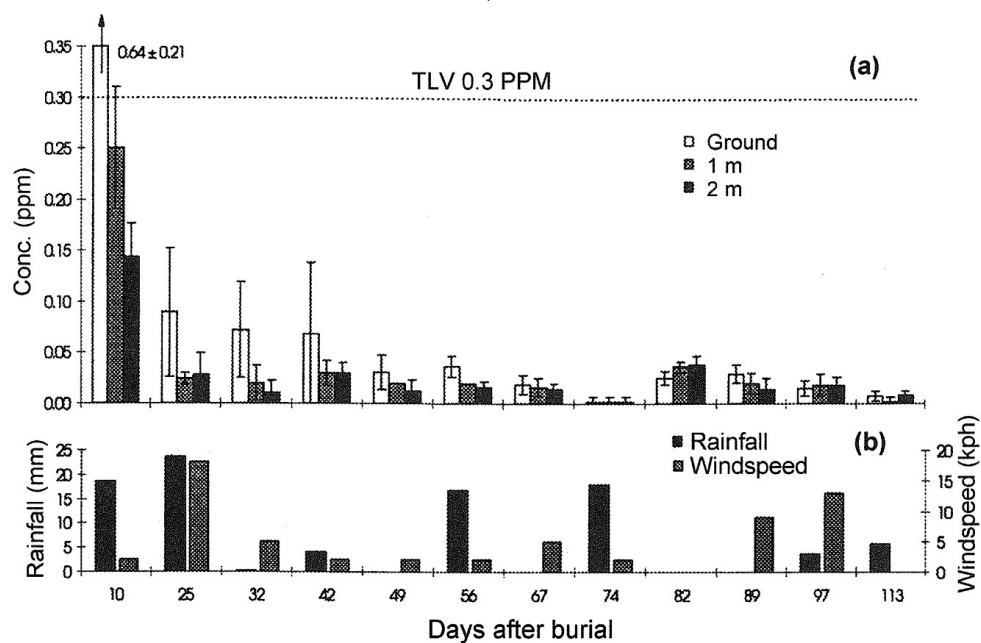


Fig. 3. Mean phosphine concentrations (\pm SD) above the test site (a) compared with windspeed on day of measurement and total rainfall for the previous 3 days (b).

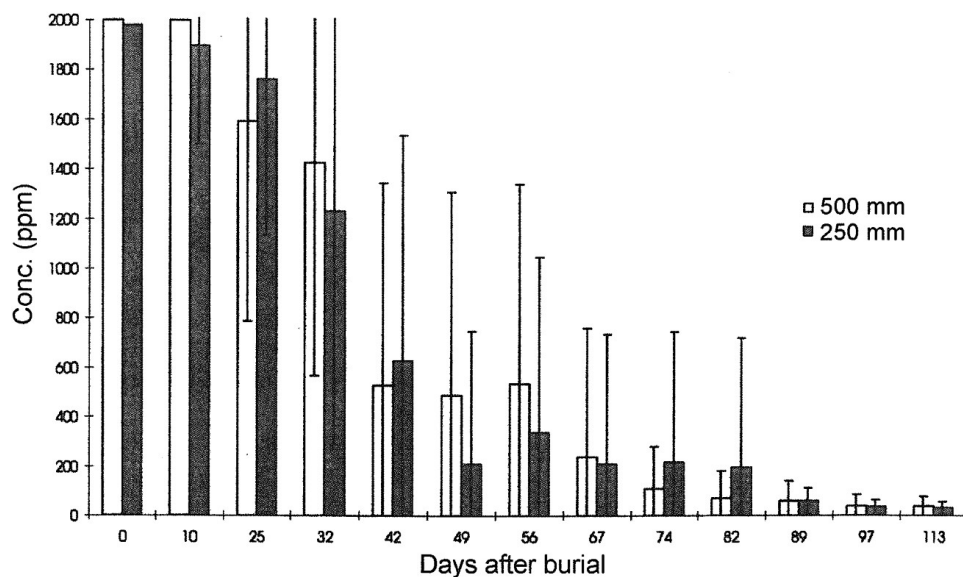


Fig. 4. Mean below-ground phosphine concentrations (\pm SD), sampled from formulations buried 250 mm and 500 mm deep.

The soil was classified as either a Dermosol (Isbell, 1994) or a Euchrozem Gn 4.12 (Northcote, 1979). These are clay soils, strongly structured and moderately deep red to reddish brown. In eastern Australia they are usually used for cropping or intensive grazing on improved pastures (Hubble *et al.*, 1983; Northcote *et al.*, 1974).

DISCUSSION

PH₃ levels measured above the burial site during the first 10 d after burial exceeded the 0.3 ppm TLV. Thereafter, no PH₃ was detected above the TLV (0.3 ppm) from ground level up to 2 m above ground level at any point across the site.

It had been expected that PH₃ levels would be affected by weather conditions at, or immediately prior to, time of measurement. In fact, these effects were not consistent. Only in some instances was there either an apparent decrease in PH₃ levels with increased windspeed or higher PH₃ levels after rain during the previous 3 d.

PH₃ levels measured below ground also appeared to be largely independent of rainfall during the observation period. From Fig. 5 it can be seen that PH₃ levels below ground decayed exponentially and could therefore be expected to reach safe levels after about 6 months. This is not to say that the same result can be expected with burial in different soil types. In the present case the soil had a high clay content; although friable and porous when dry, it could be expected to become less porous when moist, which would restrict

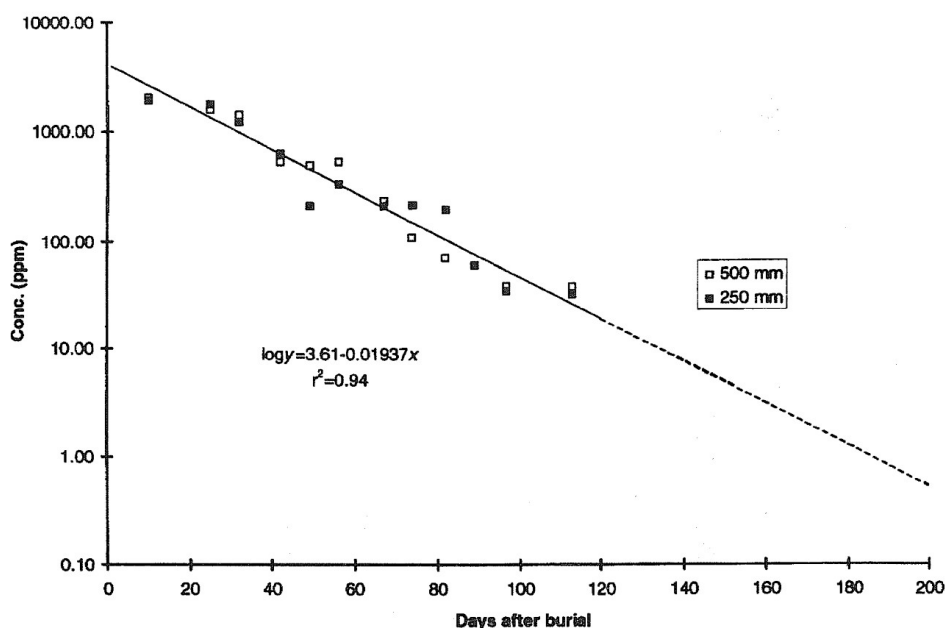


Fig. 5. Mean below-ground phosphine concentrations (ppm, log scale) showing rate of decay during the test period.

the movement of both gas and water. Disposal in sandy soils may produce different results; it would still be reasonable to expect an exponential decay but this would perhaps proceed at a faster rate.

This study is continuing, with monitoring to determine the length of time which must be allowed to pass before it is safe to unearth the buried formulations. Any future studies should include measurements of soil moisture before and during the burial period and the effect of different soil types, as well as possible effects of rain in higher rainfall areas.

CONCLUSION

If spent residues are buried as dry powder (AFHB/ACIAR, 1994), it is very likely that no PH_3 above 0.3 ppm (v/v) will be released into the environment.

In the case of unspent or partially spent AIP formulations, the work reported here indicates that PH_3 emissions immediately above the burial site remained above the TLV on day 10 but had fallen below it by day 25. Burial of these formulations resulted in lower localised levels of PH_3 in the environment than could be expected had the formulation been allowed to decompose in air. However, where this form of disposal is used it is essential to monitor PH_3 emissions to ensure that the site is safe before anyone enters the workspace. Both soil type and initial soil moisture content may also influence the rate at which PH_3 -generating formulations decompose. For this reason, access to such sites needs to be controlled in accordance with local regulations.

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