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PHOSPHINE RESIDUES REMAINING IN ALUMINIUM PHOSPHIDE PREPARATIONS AFTER BURIAL

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ABSTRACT

Recommended methods for disposal of aluminium phosphide may involve burial. A range of aluminium phosphide preparations used for fumigation consisting of partially spent, and unspent commercial phosphine (PH_3) generating aluminium phosphide formulations (blankets and sachets, pellets, and tablets), was buried for 19 months. Phosphine produced by the formulations during this period was monitored at irregular intervals.

After 19 months, samples of the buried material were retrieved. Analysis showed that material capable of generating PH_3 was still present. The results indicate that burial can reduce the amount of aluminium phosphide capable of generating PH_3 to 0.6-4.1% of the original quantity, which is similar to that found in fully spent formulations after fumigation exposures.

INTRODUCTION

There are occasions when there is a requirement for safe disposal of quantities of aluminium phosphide formulations. These may include: damaged or improperly packed products, products of uncertain age or history, and unused or partially spent (depleted) products resulting from interrupted fumigations.

Disposal procedures may involve burial of small quantities of formulation (Casa Bernardo 2000; Degesch 1999a, 1999b). However, in the case of unspent formulations, the extent and rate of decomposition of large amounts of buried formulation have not been investigated. In the present investigation a range of aluminium phosphide preparations used for fumigation of stored products was buried, and production and decay of PH_3 were observed over a period of 19 months. The buried products were then retrieved and samples analysed to determine the amount of material remaining that could still generate PH_3.

The persistence of aluminium phosphide in spent formulations is widely known but not well studied. It was reported by Winks in 1970 and has been observed by other authors (Banks, 1987; Degesch 2000; Rosebrook, 1972; Waterford *et al.,* 1994; van S. Graver and Annis 1994). This residue of aluminium phosphide is what was measured in many PH_3 residue analyses (FAO/WHO 1993) where admixture to grain was the method of application. This residue presents an OH&S issue when spent formulation is recovered for disposal, when admixture is not used. The aim of this

study was to measure the decay of aluminium phosphide as a residue when burial is used as the disposal method.

MATERIALS AND METHODS

Phosphine gas used for calibration and standardisation was prepared from aluminium phosphide tablets (Anon., 1975) and the concentration of PH_3 was determined by gas chromatography using the response of a Gowmac gas density detector. Head space concentrations of PH_3 were determined by gas chromatography using a Tracor MT220 instrument fitted with a flame photometric detector and a column of 20% SE30 on Chromosorb W.

The amount of PH_3 generating material in depleted phosphide formulations was determined by measuring the amount of PH_3 released from samples placed in dilute sulfuric acid using a modification of the method described by Pratt and Desmarchelier (1998). A weighed amount (~ 0.3 g) of each sample was placed in 25 mL of 20% sulfuric acid in a sealed Erlenmeyer flask of known volume (approx. 123 mL) fitted with a rubber septum sampling port. Phosphine concentrations in the headspace were measured periodically until the measurement became constant (24 h). The total amount of PH_3 released by a sample was estimated from the relationship between headspace concentrations and total PH_3 in flasks containing measured doses of PH_3 and 25 mL 20% sulfuric acid.

The phosphide formulations used are listed in Table 1. The formulations were buried at two depths, 250 and 500 mm with gas sampling lines as previously described (Waterford *et al.,* 1997). Phosphine produced by the buried formulations was monitored from time to time. Measurements were made at 500 and 250 mm below ground level, at ground level and 1 and 2 m above the ground. Surface and above ground measurements reduced to zero early in the burial period and were discontinued (Waterford *et al.,* 1997). After 19 months the buried formulations were retrieved. Samples were placed in air-tight plastic containers for subsequent analysis in the laboratory.

TABLE 1
Formulations used

Formulation type	Name	Condition
Blankets	Celphos® Quickphos®	Unspent and partially spent. Rolled up and unrolled. Large and small.
Pellets	Celphide®	Unspent and partially spent. Mixed origin (manufacturers).
Tablets	Phostoxin® Quickphos®	Unspent and partially spent.

RESULTS

The amount of PH_3 measured below ground declined in a predictable way (Fig. 1) and extrapolation of data obtained over the first 100 days indicated that the buried formulations should be completely spent within 250 days. However, continuing measurements showed that the below ground concentrations of PH_3 decreased to about 10 ppm and remained at that level. Analysis of samples of the phosphide formulations after 19 months of burial showed that they still contained active ingredient capable of generating amounts of PH_3 up to 4% (w/w) of the sample (Table 2).

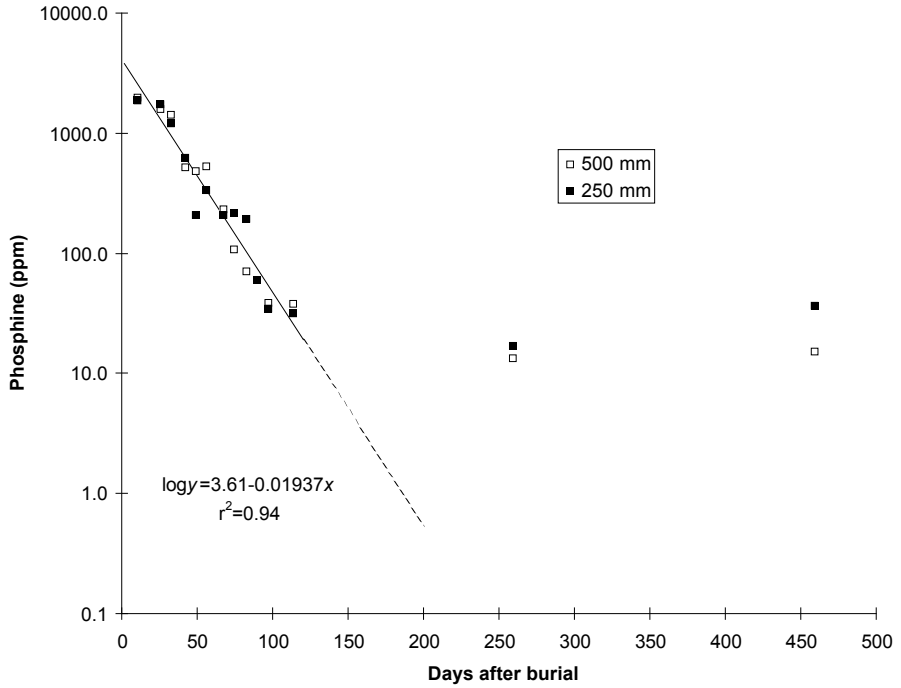

Fig. 1. Mean below-ground phosphine concentrations (ppm, log scale) showing rate of decay during 19 month burial period.

DISCUSSION

The persistence of active ingredient in the buried samples after 19 months burial was unexpected. However, the high level (4.1% PH_3) of active ingredient remaining in the Quickphos blankets may be explained by the fact that they were deliberately buried *rolled up*, as they had been in their containers. Additionally, none of the blankets had been perforated prior to burial as recommended for wet deactivation (Detia Degesch, Undated). However, the level of active ingredient remaining in the

small Quickphos blankets (0.6% PH_3) (which had been unrolled) was well below the 3-4% normally remaining in fully spent formulations after fumigation exposures.

TABLE 2
Phosphine remaining in formulations after 19 months burial

Formulation	PH_3 remaining in buried formulation (% w/w)
Quickphos blanket	3.7
Celphide pellets	2.0
Small Quickphos blankets	0.6
Phostoxin pellets	3.8
Partially spent Celphide pellets	4.0
Mixed pellets	3.2
Quickphos blanket*	3.6
Small Quickphos blanket	0.1
Quickphos blanket*	4.1

*Still rolled up when removed from container and buried.

Current recommendations for disposal of spent or partially spent, and unspent aluminium phosphide preparations involve 'dry' and 'wet' deactivation methods (Degesch 1999a, 1999b; Casa Bernardo 2000). The techniques used can involve production of considerable amounts of PH_3, which can be dangerous, causing PH_3 poisoning and physical injuries to personnel (NIOSH 1999).

Burial as a disposal option is presently limited to (i) small quantities (5-8 kg) of spent material and (ii) 'partial burial' where several "inches" of sand or soil are used to "weigh down" packaged formulations (sachets, ropes, etc.) to ensure that they are not carried away by wind during dry deactivation (Degesch 1999a, 1999b; Casa Bernardo 2000).

The study reported here indicates that the amount of unreacted active ingredient remaining in the formulation after prolonged burial can fall to levels consistent with those found in spent formulations after fumigation exposures, and after both wet and dry deactivation. Earlier work (Waterford, *et al.,* 1997) has shown that above-ground levels of PH_3 declined below the TLV within a relatively short period of time after these phosphide preparations were buried.

These results provide a single example of what can happen when aluminium phosphide preparations are buried, and may be dependent on soil type, soil moisture content, depth of burial, and total time of burial/spent underground.

Clearly more work is required to determine whether the content of active ingredient can be reduced below the levels obtained here, and how long it will take. Nevertheless, the practice of burying unwanted phosphide formulations would appear to be acceptable with regard to both environmental and safety considerations, and provide greater safety than the currently recommended procedures.

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