

## **THE CURRENT STATUS OF METHYL BROMIDE AND PHOSPHINE FUMIGATION IN POLAND**

S. IGNATOWICZ<sup>1</sup>, S. OBOZA<sup>2</sup> AND C. SLUSARSKI<sup>2</sup>

<sup>1</sup>*Warsaw Agricultural University, Department of Applied Entomology,  
Nowoursynowska 166, 02-787 Warszawa, Poland*

<sup>2</sup>*Solfum Ltd., Wojska Polskiego 83, 91-734 Lodz, Poland*

### **ABSTRACT**

Insects and mites are common pests of stored products in Poland. They not only cause economic loss of agricultural commodities in storage but, due to quarantine, their presence restricts the export of grain, dried fruits, mushrooms, vegetables and other products. These losses and restrictions are eased by the application of fumigation treatments. Only two fumigants are registered in Poland: methyl bromide (MB) and phosphine (PH<sub>3</sub>). Methyl bromide (METABROM 98; METHYL BROMIDE) is used widely as a fumigant for soils, commodities and structures. However, MB is an effective ozone-depletor and will be banned in Poland at some future date. PH<sub>3</sub> will continue to play a major role in the fumigation of agricultural commodities, and Poland is becoming increasingly dependent on this fumigant for stored-product pest control. The following PH<sub>3</sub>-releasing products are now registered in Poland: PHOSTOXIN (tablets), QUICKPHOS (pellets), DELICIA-BEUTEL (bags), DELICIA-GASTOXIN (tablets) and DEGESCH PLATES or STRIPS. For PH<sub>3</sub> to remain available as a fumigant, it is essential that any risk, such as PH<sub>3</sub>-resistance in pests, that could lead to its failure be identified and eliminated. Therefore, a research program has been undertaken to detect and monitor PH<sub>3</sub>-resistance in Poland. The information obtained will be used to predict the future impact of resistance on storage industries and to develop tactics and strategies aimed at managing or delaying the development of resistance.

### **INTRODUCTION**

Insects and mites are common pests of stored agricultural products in Poland. In some years, the acarid mites (Acaridae) alone are responsible for losses as high as 400,000 t of stored grain (Golebiowska and Nawrot, 1976). In general, 5–10% of stored commodities are destroyed by pests each year (Boczek and Ignatowicz, 1980). Stored-product pests not only cause economic loss of agricultural commodities in storage, but, due to quarantine,

their presence also restricts the export marketing of grain, dried fruits and vegetables and other agricultural products. These losses and restrictions are eased in Poland by the use of fumigation treatments with toxic gases.

All fumigants, regardless of formulation, are highly toxic and hazardous to use, and in Poland they are classified as restricted-use pesticides (Class I toxicity). A special certification, granted by the State Inspection of Plant Protection, is required from purchasers before these fumigants can be sold to them. Thus, the fumigants are only available to persons who have been certified and trained in their use (Monitor Polski, 1965). This training is periodically updated to ensure the qualifications of the person conducting a fumigation.

There are several firms and companies certified to conduct fumigation treatments of stored products in Poland, and the following firms belong to the largest fumigation companies: Agropest (Lodz), Solfum Ltd. (Lodz), Agrochemikal-Pest Ltd. (Bydgoszcz), Zakład Zwalczania Szkodników Żywności (Wrocław) and Straz Portowa (Szczecin). The Agropest company, governmentally owned since March 31, 1950, has branches and cooperating works in several regions (Białystok, Lodz, Warszawa, Krakow, Katowice, Rzeszow, Poznan, Gdynia, Radom and Klutajny near Olsztyn), and its activity covers all Polish territory. Sulfum Ltd., a private company, has branches in Opole, Gdansk and Stargard Szczeciński. In the 1990's, there emerged many small private companies which only use spraying with contact insecticides for controlling insect pests in apartments and houses.

The granary weevil (*Sitophilus granarius*), rice weevil (*S. oryzae*), flour beetles (*Tribolium* spp.), the Mediterranean flour moth (*Ephestia kuehniella*) and the acarid mites (Acaroidea) are the pests most often controlled with fumigants. The following stored products are most often fumigated: grain, processed food products, animal feed, seed for sowing, tobacco and coffee beans. 100,000 to 200,000 t/year of grain as well as structures are for the most part fumigated by Agropest, which uses approximately 3 t of metal phosphides and 60 t of MB.

Fumigation is not always practical in Poland. Grain stored in poorly sealed wooden buildings is covered with special gastight sheets. This procedure is very expensive and time-consuming. The increased amount of fumigant required and the poor control often achieved make this practice cost-prohibitive. Poor control often results in rapid resurgence of infestation which becomes just as large and damaging as before the fumigation. Therefore, small farmers, whose small, primitive storages are improperly sealed, are rarely clients of fumigation companies. One solution to this problem might be cooperatively owned and managed storages with drying facilities, but this solution is not acceptable to Polish farmers because of their bad experiences with the so-called cooperatives forced on them by the former Communist government (see also Sinha *et al.*, 1991).

Effective fumigation is possible in large grain-storage premises with good storage practices. Such storages belong to the central handling system (silos) or to flour mills, tobacco works and food processing factories.

## PAST FUMIGANT USAGE IN POLAND

After World War II, the following fumigants were used or tried in Poland: hydrogen cyanide, ethylene oxide, ethylene dibromide, ethylene dichloride and carbon tetrachloride.

In the 1950s, CARTOX (imported from West Germany) which contained 10% ethylene oxide and 90% carbon dioxide was used widely, but in 1956 it was superseded by ROTANOX, which was produced in Poland. ROTANOX was used for fumigation of structures, grain in silos, grain products in flour mills, food storages, food processing factories and, ultimately, even for desinfestation of medicinal herbs and food products in both Mallet fumigation chambers and flat storages. However, ethylene oxide was determined to be an effective carcinogenic agent and was therefore banned in Poland, in 1987, for treatment of food products. Ethylene oxide is still used in limited amounts for the fumigation of museum collections (books, carpets and wooden exhibits) and the sterilization of medical supplies (syringes and needles).

Ethylene dichloride was used only for fumigating the underfloor space of storages where other fumigants and contact insecticides were either not effective or it was impossible to apply them. No more than 10 t of ethylene dichloride was used each year. This fumigant was finally replaced by contact insecticides (DDVP) in 1982/1983.

Hydrogen cyanide was once imported from Czechoslovakia as CYJANOFUM. It consisted of calcium cyanide packed in metal tins which on reaction with water produced hydrogen cyanide. Several tons of CYJANOFUM were used yearly. In the 1960's/1970's, CYCLON was imported from West Germany in the form of filter paper imbued with liquid hydrogen cyanide which, after opening the tins in a store, quickly changed into gas form. Nine t/year of hydrogen cyanide was used for fumigation of structures and empty storages, for desinfestation of seed materials and for rodent control. It was banned in Poland in 1978–1979 both because of a possible threat to fumigators and for psychological reasons.

In the 1960's and 1970's, a wide range of gases was used in fumigation for stored-product protection in Poland (Table 1). However, in past decades there have been many pressures on particular chemicals, ranging from development of resistance by the target pests and carcinogenic concerns to increasing demands for reregistration to maintain use.

TABLE 1  
List of gas chemicals labelled for stored-product protection in Poland at the indicated years

Years	Gases used as fumigants for stored products in Poland <sup>1</sup>
1960's	hydrogen cyanide, ethylene dichloride, ethylene oxide, MB, PH <sub>3</sub>
1970's	hydrogen cyanide (1978–1979), ethylene dichloride, ethylene oxide, MB, PH <sub>3</sub>
1980's	ethylene dichloride (1982–1983), ethylene oxide (1987), MB, PH <sub>3</sub>
1990's	MB, PH <sub>3</sub>
2000's	MB (?), PH <sub>3</sub>

<sup>1</sup>Years given in the parentheses denote when fumigating stored products with a particular gas was banned.

As a result, fumigation is becoming threatened. Now only two fumigants remain in widespread use — phosphine ( $\text{PH}_3$ ) and methyl bromide (MB) (Table 2). Even these remaining materials are under pressure because of carcinogenic concerns and ozone depletion (Alavanja *et al.*, 1990; Garry *et al.*, 1989; Garry *et al.*, 1990; Ignatowicz, 1993).

TABLE 2  
Fumigants registered for fumigation of stored agricultural products  
in Poland (February 8, 1995)

Fumigant preparation	Dosage of preparation	Commodity; remarks
MB	according to instructions	grain, food products, animal feed, medicinal herbs,
METABROM 98	30–50 g/t	fabric bags; not for sowing materials or brewery
	30–50 g/m <sup>3</sup>	barley;
	20 g/m <sup>3</sup>	grain, food products, animal feed; dried fruits and
	50–100 g/m <sup>3</sup>	vegetables, medicinal herbs, food products; empty storages; fabric bags in gas chambers.
DEGESCH PLATES/STRIPS	1–3 plates/30 m <sup>3</sup>	grain and mill products, animal feed containing
	1–3 strips/600 m <sup>3</sup>	high levels of proteins and lipids; in storages, silos
	1–3 plates/15 t	and on ships.
	1–3 strips/300 t	
DELICIA-BEUTEL	2 bags/t	grain in flat storages; grain on ships.
	1.7 bag/t	
DELICIA-GASTOXIN	4–6 tablets/t	grain and raw materials for animal feed in silos;
	4–6 tablets/m <sup>3</sup>	grain, sowing materials, packed mill products,
	4–10 tablets/t	animal feed, raw materials for animal feed in flat storages; on ships.
PHOSTOXIN	4–6 tablets/t	grain and raw materials for animal feed in silos;
	4–6 tablets/m <sup>3</sup>	grain, sowing materials, packed mill products,
	4–10 tablets/t	animal feed, raw materials for animal feed in flat storages; on ships.
QUICKPHOS	20–30 pellets/t	grain and raw materials for animal feed in silos;
	20–30 pellets/m <sup>3</sup>	grain, sowing materials, packed mill products,
	20–50 pellets/t	animal feed, raw materials for animal feed in flat storages; on ships.

#### METHYL BROMIDE AND PHOSPHINE USES IN POLAND

MB is used in Poland as a fumigant for soils, commodities and structures. It is labelled for disinfestation of grain, food products, animal feed, medicinal herbs and empty fabric bags, but not for seed materials and malting barley. It is currently vital for the economic viability of certain agricultural markets and for quarantine treatment of products involved in

international trade. MB was introduced in Poland in 1964. However, long before its registration in Poland, the first field trials with MB on grain were conducted to determine and confirm its effective doses and exposure times. Initially, the use of MB was restricted to fumigation of imported grain and other agricultural products at the ports of entry. Later, its application was extended to treatment of grain and mill products, packagings (empty bags), structures, food product works and empty storages. Since 1989, it has been labelled for fumigation of medicinal herbs and soils in greenhouses and open fields.

At present, MB is successfully used by most of the fumigation companies. Up to 220 t (170 t for fumigation of structures and agricultural products and 50 t for soil fumigation) has been used each year in Poland. The Agropest company uses it for disinfestation of stored agricultural products (8–15% of tonnage) and structures (85–92% of tonnage). Solfum Ltd uses it for soil fumigation (60% of tonnage) and disinfestation of stored and transported agricultural products (40% of tonnage).

By all accounts, MB has been a very cost effective and beneficial fumigant. However, about half of the MB used as a fumigant is released into the atmosphere where it reacts with stratospheric ozone. MB has been classified as an effective ozone depletor, and because of this it will be banned at some future date (Watson, 1992; Ignatowicz, 1993). At the most recent Montreal Convention held in Vienna (1995), the developed countries decided on the following MB phase-down schedule: 25% by 2001, 50% by 2005 and 100% by 2010. The group of developing countries agreed to freeze MB use by 2002; after that year they will be limited to the 1995–1998 average yearly tonnage (ca. 220 t in Poland).

Metal phosphides will continue to play a major role in the fumigation of commodities in Poland. DELICIA (imported from East Germany) was the first preparation used in Poland which contained calcium phosphide as its active ingredient. It was packed in white paper bags within sealed metal tins containing a moisture sorbent. Before being placed in the grain, calcium phosphide was transferred into green paper bags which easily absorbed water from the surroundings. DELICIA was used only for fumigation of grain. In the 1960's, GASTOXIN was imported from East Germany in the form of tablets of aluminium phosphide (56–57%) packed in cylindrical aluminium tubes (20 tablets in a tube); there were 16 tubes in each metal tin. In the 1970's, fumigation treatments with GASTOXIN were extended to agricultural food products and seeds, and it was also used for the control of rodents. About 10 t/year of GASTOXIN were used.

At the same time, the assortment of metal phosphides was enlarged by the addition of PHOSTOXIN pellets and tablets, and later further enlarged by the addition of MAGTOXIN (a.i. magnesium phosphide). In the 1980's, another phosphide pesticide, QUICKPHOS, a product of India, was also registered. In the 1990's, two products of Detia Degesch (Laudenbach, Germany) — DEGESCH PLATES and DEGESCH STRIPS — were introduced. They contain magnesium phosphide (56%) incorporated into a plastic polyethylene matrix pressed out in the form of a flat plate and then packed in aluminium foil (Table 2).

Globally, in recent years,  $\text{PH}_3$  usage has increased considerably to more than 4,060 t/year. It has been estimated that 50% of all the grain treated with pesticides is fumigated with  $\text{PH}_3$ ; 15% is still fumigated with MB; and 35% is protected with chemical

insecticides (protectants) (Mueller, 1992). Only 60% of all metal phosphides in the United States are used for fumigation of bulk grain, whereas in Poland more than 85% of metal phosphides are used for this purpose. In 1995 the Agropest company used 60 t of MB for structures and stored products and 3 t of metal phosphides for grain fumigation. Solfum Ltd. used 110 t of MB for fumigation of soil, stored products and ships and 2 t of metal phosphides for fumigation of agricultural products.

#### **DETECTION, MONITORING AND MANAGEMENT OF PH<sub>3</sub>-RESISTANT STRAINS OF STORED-PRODUCT PESTS IN POLAND**

Poland and other countries are becoming increasingly dependent on PH<sub>3</sub> for stored-product pest control, both on-farm and in the central handling systems. PH<sub>3</sub> has many benefits over other fumigants, including ease of use, good penetration and low cost. There are few alternatives which have the same advantages, particularly with the inevitable withdrawal of MB owing to its ozone-depleting properties. In order for PH<sub>3</sub> to remain available to the industry as a fumigant, it is essential that any risk that could lead to its removal be identified and eliminated.

Entomologists involved with storage are now concerned about the potential of stored-product pests to develop PH<sub>3</sub> resistance. The FAO Global Survey of Pesticide Susceptibility indicated the potential for a PH<sub>3</sub>-resistance problem and considered that assessment of the status of PH<sub>3</sub> resistance in stored-product pests should be classed as most urgent (Champ and Dyte, 1976). Then, in the 1980's and 1990's, resistance to PH<sub>3</sub> was detected in several species of stored-grain pest insects in many countries (Subramanyam and Hagstrum, 1996).

Several surveys of PH<sub>3</sub> resistance have been performed in the US, the UK, Canada, Australia, India, the Philippines, Indonesia and Brasil (Subramanyam and Hagstrum, 1996). However, no studies have yet been initiated to monitor PH<sub>3</sub> resistance in stored-product pests in Poland. Therefore, the USDA-Warsaw Agricultural University research program on detection, monitoring and management of PH<sub>3</sub>-resistant strains of stored-product pests has been implemented in Poland.

The initial stage of the program will involve studies on baseline responses of stored-product pests in this country to PH<sub>3</sub>. Laboratory strains and field populations of stored-product pests will be tested with a range of concentrations of PH<sub>3</sub>. Concentrations that could be used with a 20-h exposure to discriminate between susceptible and resistant individuals, based on these tests, will be determined to facilitate separation of susceptible and resistant individuals in later work. Other concentrations will be determined to discriminate between the detected level of resistance and possible higher levels of resistance.

As result of this work, susceptible reference strains will be maintained, bioassay methods for rapid diagnosis of resistance will be adopted, and resistant strains from field samples will be established. These will allow the full potential of resistance to be studied and also provide material for genetical examination. Information obtained at this stage will be used in surveys on PH<sub>3</sub> resistance in field strains of pests.

One threat to the grain industry is delivery to the central handling system of  $\text{PH}_3$ -resistant strains of pests, which may develop in farm storages because of fumigations in unsealed and poorly sealed storages. It has been shown that storages in this condition are unable to meet the exposure periods required for effective control. There is much evidence to suggest that the development of  $\text{PH}_3$  resistance is associated with poor fumigation techniques (Price, 1986; Tyler *et al.*, 1983). Inefficient use of sealed silos rather than fumigation in unsealed silos, however, poses a greater threat through facilitating the development of higher levels of resistance (Emery, 1994).

In order to accurately determine the extent and level of  $\text{PH}_3$  resistance in grain pests in the central handling system's storages and on farms in Poland, a random survey will be made. The farm survey will determine the extent of  $\text{PH}_3$  resistance in Poland and facilitate the establishment of a resistance management plan which can be used to limit the development and spread of  $\text{PH}_3$ -resistant strains of grain pests.

$\text{PH}_3$  fumigation is a treatment commonly used to control pest infestations in stored commodities in Poland. However, control failures have been reported with increasing frequency and now comprise about 0.5% of all treatments. Control failures following fumigation may not always be caused by resistance. In many cases where survivors are found following treatment, the reason is improperly done fumigation, as when structures are inadequately sealed between the silo wall and the roof. The other causes of control failure include high humidity of the stored product resulting in poor gas distribution, a late decision for fumigation and low temperatures during winter treatments. The acarid mites (at hypopus stage) are relatively resistant to  $\text{PH}_3$ , and often recommended doses fail to control them. However, the frequency of existing resistance mechanisms in the pest population increases concomitantly with increasing use of  $\text{PH}_3$  fumigation. Some grain handlers therefore probably no longer use  $\text{PH}_3$  because it does not seem to work.

Following a properly conducted fumigation, control failures due to resistance depend upon both the presence of genes which confer resistance and the degree to which resistance is conferred by those genes. Zettler (1991) stated that the percentage of survivors of the discriminating dosage tests reflects only the frequency of genes for resistance in that population, telling nothing at all about the level of the population's resistance. Genes which confer resistance may occur frequently in a population without causing control failures. Thus, a strain with a high frequency of resistance might still be susceptible to normal treatments with the pesticide to which its genes confer resistance. Conversely, a strain with a low frequency of resistant individuals could be difficult to control if the few genes for resistance conferred extremely high levels of resistance. Thus, while the laboratory discriminating dose test is beneficial in detecting the early development of resistance, it plays little or no role in predicting control failures in the field.

It would be extremely useful to correlate control failures with a simple diagnostic assay for resistance. More studies are needed to evaluate not only the results of the discriminating dose tests but also such other factors as the level or intensity of resistance in a particular population. The results may explain the cause of the control failures with  $\text{PH}_3$ ; they will certainly help in making pest control decisions.



The last stage of this study will be to establish the cross-resistance characteristics of resistance. This will involve selecting the resistant population in the laboratory with the failing chemical (PH<sub>3</sub>) until all (or most) individuals in the population are homozygous for the resistance mechanism. Such selection is necessary because new resistances can be associated with a loss of fitness so that resistance levels may be lost during culturing, selection of the resistant population allows the full potential of the resistance to be measured, and selection provides the material needed for more detailed genetic studies (Collins, 1990).

The response of the resistant strain to a wide range of chemicals, including new fumigants such as carbonyl sulphide and protectants registered for use on grain, such as ACTELLIC 500 EC or K-OBIOL 25 EC, will then be tested. The results will show which insecticides are jeopardised by resistance and which are not; they will also provide a reasonable indication of the field doses necessary both to kill adults and to prevent the development of progeny (i.e. if any cross-resistance is provoked by PH<sub>3</sub>-resistance).

Results of this project are expected to provide immediate benefit to Polish pest-management programs, none of which presently incorporate resistance management. Thus, pest control efficiency should increase immediately and, with resistance management practices in place, improved control efficiency will be maintained in the future despite increasing levels of resistance. Finally, the development of pest management programs in relation to worldwide resistance will have a positive influence on grain exports/imports.

#### ACKNOWLEDGEMENTS

The paper was prepared with the financial support of the US–Poland Maria Skłodowska-Curie Joint Fund II (Project MR/USDA-96-235). The authors acknowledge this financial support.

#### REFERENCES

- Alavanja, M.C.R., Blair, A. and Masters, M.N. (1990) Cancer mortality in the US flour industry. *J. Ntl. Cancer Inst.* **82**, 840–848.
- Boczek, J. and Ignatowicz, S. (1980) Straty powodowane przez szkodniki przechowywanych produktów na świecie i w Polsce [Losses caused by stored product pests in the world and in Poland]. *Ochrona Roslin* **24** (10–11), 16–18.
- Champ, B.R. and Dyte, E.E. (1976) *Report of the FAO Global Survey of Pesticide Susceptibility of Stored Grain Pests*. FAO Plant Protection Service, **5**, Rome, Italy.
- Collins, P.J. (1990) Management of resistance to insecticides in stored grain: Resistance risk and impact assessment. In: *Proc. 5th Int. Working Conf. on Stored-Product Protection* (Edited by Fleurat-Lessard, F. and Ducom, P.), Bordeaux, France, 9–14 September 1990, **2**, 983–988.
- Emery, R.N. (1994) A Western Australian farm survey for phosphine resistant grain beetles. In: *Proc. 6th Int. Working Conf. on Stored-Product Protection* (Edited by Highley, E., Wright, E.J., Banks, H.J. and Champ, B.R.), Canberra, Australia, 17–23 April 1994, CAB International, Wallingford, Oxon, UK, **1**, 98–103.



- Garry, V.F., Griffith, J., Danzl, T.J., Nelson, R.L., Whorton, E.B., Krueger, L.A. and Cervenka, J. (1989) Human genotoxicity: pesticide applicators and phosphine. *Science* **246**, 251–255.
- Garry, V.F., Nelson, R.L., Griffith, J. and Haskins, M. (1990) Preparation of human study of pesticide applicators: sister chromatid exchanges and chromosome aberrations in cultured human lymphocytes exposed to selected fumigants. *Teratogenesis, Carcinogenesis, and Mutagenesis* **10**, 21–29.
- Golebiowska, Z. and Nawrot, J. (1976) *Szkodniki magazynowe* [Stored product pests]. PWRiL, Warszawa. 274 pp.
- Ignatowicz, S. (1993) Bromek metylu niszczy warstwę ozonową w stratosferze [Methyl bromide depletes the stratospheric ozone]. *Ochrona Roslin* **37** (7), 19–20.
- Monitor Polski (1965) Zarządzenie Ministra Rolnictwa z dnia 22 kwietnia 1965 r. *Mon. Polski*, poz. 156, par. 17, pkt. 2.
- Mueller, D. (1992) An alternative to methyl bromide in stored product. *Fumigants and Pheromones* **31**, 5.
- Price, N.R. (1986) The biochemical action of phosphine in insects and mechanisms of resistance. In: *Proc. Group for Assistance on Systems Relating to Grain after Harvest, Seminar on Fumigation Technology in Developing Countries*, 18–21 March 1986. TDRI, London, 99–104.
- Sinha, R.N., Muir, W.E. and Sellen, R.A. (1991) Cereal storage loss study Poland mission — summer 1990. *Int. Agr. Dev., Int. Prog. Br., Agriculture Canada, Ottawa. Tech. Report*, 1–24.
- Subramanyan, B. and Hagstrum, D.W. (1996) Resistance measurement and management. In: *Integrated Management of Insects in Stored Products* (Edited by Subramanyan, B. and Hagstrum, D.W.), Marcel Dekker, Inc., New York-Basel-Hong Kong, 331–397.
- Tyler, H.J., Taylor, R.W. and Rees, D.P. (1983) Insect resistance to phosphine fumigation in food warehouses in Bangladesh. *Int. Pest Control* **25**, 10–13.
- Watson, R. (1992) Methyl bromide and the ozone layer: a summary of current understanding. Paper presented at the 1992 Fumigants and Pheromones Technical Seminar, Indianapolis, Ind., USA.
- Zettler, J.L. (1991) Phosphine resistance in stored product insects in the United States. In: *Proc. 5th Int. Working Conf. on Stored-Product Protection* (Edited by Fleurat-Lessard, F. and Ducom, P.), Bordeaux, France, 9–14 September 1990, **2**, 1075–1082.