Needs for R & D in Fumigation and Controlled Atmospheres for Grain Storage

H.J. Banks*

Abstract

The main limitations for fumigation, at present, concern public health and environmental laws, and length of treatment time, and, for CA, cost and speed of action. Research needs to be aimed at overcoming these limitations if the technology is to progress. Controlled atmospheres are being considered as one of the alternatives to fumigation. With increasing concern over the possible effects of many chemicals, including fumigants, there is pressure to provide data to justify and improve existing fumigation practices, and to reduce the perceived and real potential hazards of use of highly toxic fumigants. There is a need to coordinate effort on environmental and public health aspects of fumigants internationally so appropriate data can be gathered quickly and avoid precipitate restriction or removal of these valuable materials from use. It is likely that there will be introduced, in the near future, a requirement for both personal monitors for workers close to fumigations and for scrubbers to remove fumigant from exhaust gases after treatments. The need for more rapid turnaround will force a reevaluation of fumigant regimes, perhaps leading to shorter treatments at higher dosages, particularly with methyl bromide. Reevaluation of currently permitted but nevertheless neglected fumigants — hydrogen cyanide and the formates — is overdue. CA research needs to provide means of creating and maintaining atmospheres cheaply and increasing their speed of action, particularly at low temperatures. The use of membranes, propane burners, and chemical absorbers for making low-cost, oxygen-deficient atmospheres on-site all show promise. There is a need for further research to define the limits of action of various atmospheres against specific pests and to develop systems for storage of intermediate moisture content (14-18%) grain.

FUMIGATION and controlled atmospheres (CA) are mature technologies. Both have been subject to much research and development (R & D) and are at a stage where application is largely routine. Opportunities for further development appear limited. Yet even now both techniques face some challenges. Fumigation in particular is under pressure from increasing restriction driven by concerns over public health and the environment, and the reaction of both markets and workers to the use of highly toxic chemicals.

In some countries, e.g. West Germany, fumigations are so constrained by regulation as to be difficult to carry out, while in others, notably USA, the threat of litigation over possible effects of fumigants has led some industries to discontinue their use. Controlled atmospheres are now being considered as alternatives to fumigation. However, they are less convenient and familiar, and need some further development, particularly to reduce associated capital costs, before they can be regarded as competitive in most sit-

---

* CSIRO Division of Entomology, GPO Box 1700, Canberra, ACT 2601, Australia

uations. This paper summarises the R & D needs for both fumigation and CA as applied to grain and, perhaps just as importantly, gives topics on which effort no longer seems required. A related analysis, focusing particularly on the needs for R & D for fumigation in the humid tropics, was given recently by Banks (1987). Note that there are many background data and development results available on CA and fumigation, though this may not always be recognised or easily accessible, with consequent wasteful duplication of effort. There is often more to be gained from efficient information retrieval and assimilation than from carrying out new trials or experiments. There is a continuing need for topical and thorough reviews to collect the widely dispersed data on particular aspects of fumigation and CA.

Research on gas processes as a means of grain preservation should be kept in perspective. Usually the objective is better pest control in stored grain rather than better fumigation. Gas processes are but one of many approaches that can be used to help achieve the basic aims of grain storage, providing a system that keeps grain adequately, given the economic and strategic constraints of the situation. The categories of grain preservation and disinfestation techniques available are summarised in Table 1. Gas processes are unique in that they can achieve complete disinfestation from pests in a short time and without moving the grain. Nevertheless, other techniques or combinations thereof, may give adequate protection and possibly at a lower cost. On the other hand, use of fumigation or CA may often be the optimum way of dealing with a particular situation.

Despite the foregoing considerations, there are several avenues of research related to CA and fumigation that appear worth pursuing. Some, notably those concerned with environmental and public health aspects, must be urgently addressed if sudden restrictions on the use of fumigants in particular are to be avoided. The research areas needing attention can be summarised thus:

Enabling technologies for both CA and fumigation	– sealing and storage design – flow through techniques – action levels
Fumigation-specific problems	– basic parameter estimation – rates of formation and definition of residues – biological activity, including ways of enhancement – effect on processing and end use parameters – monitoring, public health and environmental concerns – quarantine – replacement fumigants
Controlled atmospheres problems	– gas supply systems – effect on processing and end use parameters – enhancement of action

Enabling Technologies and Common Problems

Both CA and fumigation rely on containment of gases within an enclosure for sufficient time to effect the desired action, be it pest control, mould control, or grain quality preservation. Both have similar basic needs in terms of structures and are subject to the same set of constraints in terms of gas behaviour. The main differences are associated with the toxicity of fumigant chemicals to humans and the possibilities for quality protection. Common problems are discussed first in this section, followed by a consideration of problems specific to either fumigation or CA.

Sealing of Enclosures; Flow-through Techniques

It is well recognised that treatment enclosures must be sealed to some extent. Permanent sealing of many storage types is now routine (Ripp et al. 1984) and well-sealed enclosures for bag stacks are easily made (Annis and Graver 1986; Annis et al. 1984). Some development work is needed to determine optimum sealing pro-

Table 1. Processes for insect control in stored grain

Biological control
Chemical protectants and growth regulators
Drying and use of aridity
Exclusion
Gas processes — fumigation and CA
Heating and cooling
Insect-resistant varieties
Irradiation (ionising)
Physical removal and hygiene
Shock and impact
Trapping

cesses, including consideration of availability of materials and skills for particular local conditions. The level of sealing required to guarantee a high probability of successful treatment, given otherwise adequate dosing and distribution, lies in the range given by pressure decay times (pressure halving) of 3–15 minutes (Banks and Annis 1984; Annis 1990), with 5 minutes a typical specification. Many structures that do not achieve this level are treated, with the inevitable risk of control failure. Data are needed on the balance between sealing effort and cost to achieve a satisfactory standard, and on the costs incurred in failures (retreatment costs, resistance selection, commodity damage, safety risks, etc.). Without this background, statements such as 'sealing is expensive' are meaningless.

Two approaches have been made towards reducing the level of sealing required, the 'flow-through' technique (Winks 1986) and the multiple dosing technique (Friendship et al. 1986). The flow-through technique relies on continuous addition of gas to counteract the tendency of air to enter leaks and to replace any lost fumigant. In theory it should be possible to add gas at such a rate that pressures across leaks are always positive with respect to the external environment and so no leakage in occurs. Except in well-sealed systems the costs of this are prohibitive and 'flow-through' systems depend on a fluctuating concentration of active agent close to the leaks. Flow-through systems, common in CA (Banks and Annis 1977; Jay 1980), have recently been applied to phosphine fumigation (Winks 1986). Multiple dosing, a compromise between 'one-shot' and 'flow-through', attempts — by repeated addition of new fumigant — to maintain concentration in the face of leakage. The known physics of gas leakage into stores (Banks and Annis 1984) leave no doubt that, at some level of leakiness, failures using these techniques are very probable. Research is required to quantify the expected failure rate for given situations and levels of sealing, thus providing a basis for standards for these methods.

Action Levels

A problem common to both CA and fumigation is the definition of action levels — levels of infestation at which a control treatment should be undertaken. In warm climates, there is a very high likelihood that grain taken into store from the producer and most handlers will carry infestation. Where the market operates on the basis of a nil tolerance, i.e. no detectable pest infestation, there is little doubt that control measures should be applied when the grain is taken into store. Thus, in Australia, almost all grain taken into large bulk storage is treated within two months of receipt.

Where some infestation and damage are acceptable to the end user, the problem is more complex. As yet, there is no recognised standard that gives a guide to when fumigation or CA disinfestation should be applied, though this is clearly required. However, it will need to combine considerations of cost, the potential risk, pest numbers, the favourability of the environment for pest proliferation, and end-user requirements.

An action level of 20 insects per tonne for storage periods of less than six weeks in tropical situations has been recommended (AFHB–ACIAR 1989). However, it may well be that the correct approach, in most cases, will be to apply a treatment regardless of whether infestation is detected or not, rather than adopt a complex decision-making process.

Fumigation — Problems Requiring R & D

Basic Parameter Definition, Value Estimation, and Modelling

The processes underlying the interaction of fumigants and grain are discussed in another paper in these proceedings (Banks 1990). There is a need to define and quantify these processes to provide a better understanding and give well-based input into mathematical models of fumigation processes. Properly developed models should allow design predictions of the likely course of events in untried situations (e.g. residue formation at untested temperatures; different grain types; moisture or fumigant distribution in unfamiliar structures) without the need for much full-scale trial work.

A major problem outstanding in fumigation is the elucidation of the chemical pathways leading to residue formation in grains for even the most common fumigants, methyl bromide and phosphine. Residue studies for methyl bromide have largely concentrated on observing the fate of the easily observed bromide moiety, ignoring the fate of the methyl group. The research underpinning the current perception of where the methyl group goes relates almost entirely to one study on wheaten flour (Winteringham et al. 1955). There are very few data on whole grains (but see Shiroishi et al. 1961). Opinions on the fate of phosphine (Anon. 1988) rely largely on studies on artificial substrates and the erroneous belief that either no residues are formed or, if they are, they consist of phosphorus oxyacids only. However, there are indications that the situation may not be so simple. Phosphine, despite its volatility, can be retained for long periods on grain (Dumas 1980), suggesting some reversible chemisorption, possibly leading to further reaction, and there are indications that at least part of the phosphine taken up becomes bound to protein in some form (Tkachuk 1972). There are no data on the alteration products made when phosphine reacts with grain constituents. Without knowledge of the pathways involved in chemisorption, and reaction measurements of some fundamental features, understanding of fumigant behaviour towards grain must remain empirical, with the danger that conclusions drawn may not apply to new situations, such as unfamiliar conditions, grains, or even grain varieties.

There is much work to be done on measurement of the kinetics of fumigant interaction with grains and similar commodities. In particular, the rates of diffusion and reaction of fumigants in grain, and sorption isotherms on grains should be determined. However, there is always the chance that, given our imperfect knowledge of the controlling mechanisms, effort will be misdirected and measurements will need to be repeated in the light of new information. It is to be hoped that some unifying principles will be discovered that will avoid the need to study, in detail, each grain and set of conditions. Some examples of this approach have already been reviewed by Banks (1986a). The processes underlying sorption and desorption must be properly defined. They can then presumably be incorporated into models that are likely to reliably predict real fumigant behaviour in real situations. At present, construction of complex models to predict gas behaviour, such as during venting or convective transfer, seems both premature and dangerous. They may result in conclusions that are limited at best, but may even be misleading.

Biological Response to Fumigants and Increasing Speed of Action

The biological response of at least the common grain pests to the common fumigants at fixed concentrations is now known (Hole et al. 1976; Bond 1984; Price and Mills 1988). However, some further work may be required to determine the response of minor pests and to monitor resistance development. The main problem is how to fit the known laboratory-determined generalities into practice. Close investigation of the response of insect pests to phosphine has come up with some unpalatable results, notably that phosphine may be ineffective when applied for short periods (Winks 1986), and this problem becomes more acute at lower temperatures. A way of enhancing the toxicity so exposure periods could be reduced would certainly be useful.

There is often an economic advantage in being able to carry out a disinfestation rapidly. With the current pressures to optimise throughput and utilisation of facilities, it is likely that fumigant schedules will need to be reevaluated. There appears to be no way that exposure times for phosphine can be reduced from the quite long periods required for complete disinfestation (7 days at 25°C), apart from preheating the grain mass as suggested by Jay (1986). Claims that some phosphine-producing formulations can give shorter effective exposure periods appear to be unfounded. However, with methyl bromide, short exposure periods do appear to be feasible because, for the same Ct-product, concentrations for short exposures are more effective than low concentrations for long times. The main constraints to carrying out methyl bromide fumigation rapidly thus appear to be distribution and removal of the gas after a treatment rather than toxicology, and research should concentrate on optimising the former factors.

There is a need for data on the response of pests to varying concentrations of fumigant, particularly phosphine, so as to be able to relate laboratory data with the normal concentration–time variation found in practice. When a fumigation is carried out in a partially sealed system, regions close to leaks may be subjected to fluctuating concentrations. In most treatments the concentration of fumigant falls with time as a result of sorption and leakage after the initial charge has become distributed. It has yet to be fully demonstrated how effective such concentrations are and what effect they have on behaviour and development. It may be that some pests can avoid the action of the fumigant either by movement, or alteration of development so that a tolerant phase or state is prolonged. Fluctuating concentrations may or may not have advantages over the normal fixed or falling concentrations. There are indications that the rapid rise and then slow fall of concentration, typical of a good phosphine treatment, may be less effective than a constant concentration (Reichmuth 1986). However, this has as yet to be shown for the pupal and egg stages, the developmental stages most tolerant of phosphine and thus most likely to survive treatments.

End-Use Parameters

The effect of fumigants on end-use parameters is a strangely neglected field of research. With the exception of data for the effects of fumigants on the milling and bread-making quality of wheat, there is little information available (but see Taylor 1975; Banks 1981). Data are particularly scarce for tropical grains and cultural practices, and where grain is stored hot and possibly close to or above normal safe moisture limits. Systematic studies are required on the effect of fumigants on end-use qualities such as germination, yield from treated seed, and texture and acceptability of cooked products such as grits, boiled rice, and many oilseeds. Current indications suggest that neither phosphine nor methyl bromide cause unacceptable changes in processing and organoleptic qualities of products derived from treated grains, but methyl bromide may often affect germination. Some cultivars may even be sensitive to phosphine (Joubert and du Toit 1969; Kamel et al. 1974).

Quarantine Treatments

Quarantine treatments must be highly reliable. At present, methyl bromide is almost always specified as the fumigant for such treatments. This is despite data suggesting particular target organisms would be better controlled by other agents (e.g. *Trogoderma granarium* with phosphine (Bell et al. 1984)) and the need for exceptional dosage rates (e.g. 120 g/m^3 against the snail *Achatina fulica* (Bond 1984)) with the likelihood that a single treatment may give bromide residues exceeding normally permitted tolerances. There is an urgent need to undertake the tests necessary to substantiate alternative fumigants (or other processes) as acceptable quarantine treatments.

Environmental and Worker Safety Considerations

Increasing public and worker awareness and concern over use of chemicals in almost all forms makes it inevitable that highly toxic fumigants will be scrutinised finely, and there will be increasing regulatory pressure and accountability in their application. In particular, there may well be a need for personal monitors to record and quantify exposure or prove non-exposure of persons in the vicinity of fumigation, and for stationary process monitors to record and control emissions of fumigant. Devices must be both specific and cheap. At present there are no machines available that will provide a dosimeter-type record of exposure for either methyl bromide or phosphine that are sensitive enough to record below current hygienic standards. Generally, the apparatus available for measuring fumigant concentrations is inadequate, and improved systems are urgently needed. Of the machines available for methyl bromide monitoring, only indicator tubes distinguish between methyl bromide and methyl chloride. The others (e.g. infrared detector, simple gas chromatograph) record a composite of the two gases. Devices recently described for phosphine monitoring are either not continuous (Harris 1986) or apparently unavailable commercially (Ducom and Bourges 1986).

A possible solution to the concern over emission of fumigants directly into the atmosphere is to conduct treatments only in enclosures that are very well sealed and thus reliably contain the fumigant. At the end of the fumigation period, the atmosphere in the enclosure would be vented through some system that absorbs or decomposes the fumigant in the exhaust gas. To my knowledge, no such device that could be fitted to grain storages at an acceptable cost has yet been developed for either phosphine or methyl bromide.

There is an urgent need to provide well-substantiated information on the fate of fumigants in the atmosphere. It is said that both methyl bromide and phosphine break down quickly in free air. However, the studies on which these conclusions are based (Castro and Belser 1981; Fritz et al. 1982) were conducted using ultraviolet radiation of wavelengths shorter than present naturally in the lower atmosphere, and much longer half-lives than the few hours suggested may be expected around fumigation areas.

New and Old Fumigants

The choice of fumigants for grain is very restricted. In practice usually only two — methyl bromide and phosphine — are considered. Research is needed to broaden this choice so that, should one or both of these no longer be available for some reason (e.g. supply, consumer preference, insect resistance, regulatory restriction, etc.), others may immediately be available. The choice may be widened either by development of new fumigants or resurrection of discarded materials. It is often said that there can be no new fumigants, as a fumigant must be highly volatile and simple chemistry restricts the choice to small molecules composed of light elements only. Most of the possible volatile compounds have already been tested and found inappropriate for some reason. While the perceived need for high volatility may not be correct — a case can be made for highly toxic but rapidly degradable materials of low volatility as fumigants (Banks and Desmarchelier 1979) — it is undoubtedly true that the choice is very limited. Even if an alternative fumigant were selected, the required testing and registration procedures would present a formidable barrier to its adoption and use. Materials formerly used as fumigants, and currently discontinued or overlooked — notably the formates and hydrogen cyanide — appear to have more promise. Such materials need reassessment in the light of modern techniques of application and use, and residue requirements. Their biological activity may also need reinvestigation to a standard where it is comparable with that for methyl bromide and phosphine. Their spectra of action against immature stages, for instance, are not well defined.

Controlled Atmospheres

There are three main outstanding problems in CA technology:

- atmosphere generation technology;
- definition and enhancement of biological action; and
- effect on end use parameters

General CA technology has been developed to a level where it is ready for commercial use requiring little adaptation to meet local requirements. Its use is largely constrained by cost, the need to adapt storages, and unfamiliarity with the technique. The slow speed of action can also restrict use.

Atmosphere Generation Technology

Significant progress has been made recently towards replacing the use of tanker gases, often both inconvenient and expensive at remote sites, with systems of on-site generation of CA. There is now a choice of processes available for on-site production of gas for CA (Banks 1984), including membrane separation systems, pressure-swing absorption systems and burners. All of these are capital intensive, and complex pieces of equipment and further development is required to reduce costs or provide cheaper alternatives. Some alternatives have already been suggested (Banks 1984). The biological systems relying on metabolism to remove oxygen seem attractive in their simplicity but have yet to be demonstrated on a large scale. Chemical absorbers such as the iron-based 'Ageless' also show promise (Ohguchi et al. 1983). It may be that a combination of oxygen removers and metabolic action of the grain could give a modern form of hermetic storage.

Biological Activity

The overall picture of the response of coleopterous pests of grain to various CAs is now reasonably well known (Annis 1987; Reichmuth 1987), though there is still some uncertainty as to the role of CO_2 in low oxygen atmospheres, and the temperature dependency of many CAs could be better defined. Data on the action of CAs on mites and other invertebrate grain pests, e.g. psocids, indicate that CAs can affect them (Bailey and Banks 1980; Navarro et al. 1985; Leong and Ho 1990) but systematic studies are not available. The effects on moulds vary widely with the target species and strain and particular atmosphere used, and further detail is required on mould control and associated toxins at both the laboratory and field scale .

The slow action of CAs at low storage temperatures (< 20°C) is a major hindrance to use of the technique. Methods to enhance the speed of action at low temperatures would be most welcome.

Quality Effects

The effects of CAs on various quality and end-use parameters are reviewed in another paper in these proceedings (Gras 1990). In general, under relative humidities of less than about 70% and storage temperatures below 35°C, little or no effect is observed. However, at intermediate moisture contents (14–18% for wheat) there can be some beneficial effects on quality retention compared with grain stored in air. The effects are usually small in comparison with benefits obtained by reducing moisture content or temperature, but may nevertheless be useful in specialised situations. The application of CAs in otherwise marginal storage conditions seems to merit further research and development. CO_2–air mixtures and atmospheres with very low oxygen content (< 0.3%) show particular promise for inhibiting spoilage.

Combination

Study of the effect of combinations of fumigation and CA and other processes continues to hold promise as a means of enhancing action against pests, despite lack of positive effect of phosphine with methyl bromide (Bond and Morse 1982), and only partial success with phosphine with CO_2 (Desmarchelier 1984). Use of CO_2 as a carrier gas for fumigant is now well demonstrated (Navarro 1986; Hah et al. 1981; Banks 1986b) and application of CA with heat seems to be a good alternative to fumigation for some insect control (Jay 1986). The observation by Buscarlet et al. (1987) that nitrogen CA rapidly kills insects after irradiation is most interesting and worthy of further investigation, as it may solve one of the main drawbacks to the use of radiation, namely the presence of live, but sterile, insects after treatment. The combination of disinfestation by gases with use of a permanently sealed insect-resistant enclosure is well known (Banks and Ripp 1984; Annis and Graver 1986). There is a need for extension of this technique with provision of cooling in some way to enhance the storability of sensitive commodities such as moist grains, or where retention of very high levels of germination is required.

Conclusion

This paper has attempted to highlight particular areas of concern and ignorance with regard to fumigation and CA. The most urgent problems for fumigants are associated with the understanding of environmental effects, public health implications and residue problems. For CA, there is a particular need to develop and prove systems that generate and maintain the required gas mixture at low cost.

New demands for information on the effects of fumigants are likely driven by the general trend to scrutinise closely the use of chemical control methods, and the public perception that use of chemicals on foodstuffs is to be avoided. Obviously, it will be important for research workers to anticipate and gather appropriate data to meet such demands. Some conflicting requirements are already present and more are likely to arise. In particular, there is a problem that a material may become banned for use in some industrialised countries for what may seem minor defects when viewed in the context of its use in poorer areas. In the latter, food supply is a critical priority and the recorded adverse effects may not be regarded as significant. However, the decisions in the sophisticated markets will certainly influence use elsewhere via requirements for treatment of commodities in international trade. It follows that researchers everywhere should at least take note of trends in regulations and usage in regions such as Europe and North America when planning research work on fumigants.

With efficiently applied effort, particularly in the areas of environmental and public health concern, it should be possible to anticipate the demands of regulatory authorities with regard to fumigants. This should avoid the sudden loss of either of our two remaining widely-used fumigants, phosphine and methyl bromide, as a result of lack of appropriate data, rather than from a demonstration of unforeseen adverse effects. At present, research work on fumigants is conducted at a national level though, in view of the breadth and complexity of the task, it seems appropriate that there be some international coordination of this effort to ensure that both critical problems are addressed and that scarce resources are well employed.

Controlled atmosphere techniques appear to be in a much less vulnerable position than fumigants. However, it must be remembered that, as used against insect pests, the atmospheres are lethal to humans and doubtless there will be increasing regulation of CA. Nevertheless, even now CA appears to present a reasonable alternative to fumigation, at least at high storage temperatures.

It is to be hoped that further research in fumigation and CA will provide no unpleasant surprises and that use of gases will continue to provide efficient pest control in stored grain.

References

AFHB–ACIAR 1989. Suggested recommendations for the fumigation of grain in the ASEAN region. Part 1. Principles and general practice. Kuala Lumpur, AFHB; Canberra, ACIAR. 139 p.

Anon, 1988. Phosphine and selected metal phosphides. Environmental Health Criteria 73. Geneva, World Health Organization.

Annis, P.C. 1987. Towards rational controlled atmosphere dosage schedules: a review of current knowledge. Proceedings of the 4th International Working Conference on Stored-product Protection, Tel-Aviv, 128–148.

Annis, P.C. 1990. Sealed storage of bag stacks: status of the technology. These proceedings.

Annis, P.C., Banks, H.J., and Sukardi, 1984. Insect control in stacks of bagged rice using carbon dioxide treatment and an experimental PVC-membrane enclosure. CSIRO Australia Division of Entomology Technical Paper No. 22, 38 p.

Annis, P.C., and Graver, J. van S. 1986. Use of carbon dioxide and sealed storage to control insects in bagged grain and similar commodities. In: Champ, B.R., and Highley, E., ed., Pesticides and humid tropical grain storage systems: proceedings of an international seminar, Manila, Philippines, 27–30 May 1985. ACIAR Proceedings No. 14, 313–321.

Bailey, S. W., and Banks, H. J. 1980. A review of recent studies of the effects of controlled atmospheres on stored product pests. In: Shejbal, J., ed., Controlled atmosphere storage of grains. Amsterdam, Elsevier, 101–118.

Banks, H. J. 1981. Effects of controlled atmosphere storage on grain quality — a review. Food Technology in Australia, 33, 335–340.

Banks, H. J. 1984. Current methods and potential systems for production of controlled atmospheres in grain storage. In: Ripp, B.E. et al, ed., Controlled atmosphere and fumigation in grain storages. Amsterdam, Elsevier, 523-542.

Banks, H. J. 1986a. Sorption and desorption of fumigants on grains: mathematical descriptions. In: Champ, B.R., and Highley, E., ed., Pesticides and humid tropical grain storage systems: proceedings of an international seminar, Manila, Philippines, 27–30 May 1985.ACIAR Proceedings No. 14, 179–193.

Banks, H. J. 1986b. The application of fumigants for the disinfestation of grain and related products. In: Champ, B.R., and Highley, E., ed., Pesticides and humid tropical grain storage systems: proceedings of an international seminar, Manila, Philippines, 27–30 May 1985. ACIAR Proceedings No. 14, 291-298.

Banks, H. J. 1987. Research and development opportunities for fumigation in the ASEAN region as a component of integrated commodity management. In: Evans, D.E., and Wellisch, P.K., ed., Grain storage in ASEAN: some research and development options. CSIRO Australia Division of Entomology report No. 42, 29–35.

Banks, H. J. 1990. Behaviour of gases in grain storages. These proceedings.

Banks, H. J., and Annis, P. C. 1977. Suggested procedures for controlled atmosphere storage of dry grain. CSIRO Australia Division of Entomology Technical Paper No. 13, 1–23.

Banks, H.J., and Annis, P. C. 1984. Importance of processes of natural ventilation to fumigation and controlled atmosphere storage. In: Ripp, B.E. et al., ed., Controlled atmosphere and fumigation in grain storages. Amsterdam, Elsevier, 299–323.

Banks, H.J., and Desmarchelier, J. M. 1979. Chemical requirements for a fumigant to be used in partially sealed enclosures. In: Evans, D.E., ed., Australian contributions to the symposium on the protection of grain against insect damage during storage, Moscow, 1978. Canberra, CSIRO Australia Division of Entomology, 92–98.

Banks, H. J., and Ripp, B. E. 1984. Sealing of grain storages for use with fumigants and controlled atmospheres. Proceedings of the 3rd International Working Conference on Stored-product Entomology, Manhattan, Kansas, 375–390.

Bell, C. H., Wilson, S. M., and Banks, H. J. 1984. Studies on the toxicity of phosphine to tolerant stages of *Trogoderma granarium* Everts (Coleoptera, Dermestidae). Journal of Stored Products Research, 20, 111–117.

Bond, E. J. 1984. Manual of fumigation for insect control. Rome, FAO. 345 p.

Bond, E. J., and Morse, P. M., 1982. Joint action of methyl bromide and phosphine on *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae). Journal of Stored Products Research, 18, 83-94.

Buscarlet, L. A., Aminian, B., and Bali, C. 1987. Effect of irradiation and exposure to nitrogen on mortality of adults of *Tribolium confusum* J. du V. Proceedings of the 4th Working Conference on Stored-Product Protection, Tel Aviv, Israel, 186-193.

Castro, C. E., and Belser, N. O. 1981. Photohydrolysis of methyl bromide and chloropicrin. Journal of Agricultural and Food Chemistry, 29, 1005–1008.

Desmarchelier, J. M. 1984. Effect of carbon dioxide on the efficacy of phosphine against different stored product insects. Mitteilungen aus der Biologischen Bundesanstalt für Land-und Forstwirtschaft, 220, 1–57.

Ducom, P., and Bourges, C., 1986. A new technique for the measurement of phosphine concentrations. In: GASGA Seminar on Fumigation Technology in Developing Countries, Tropical Development and Research Institute, Slough, 66-73.

Dumas, T. 1980. Phosphine sorption and desorption by stored wheat and corn. Journal of Agricultural and Food Chemistry, 28, 337–339.

Friendship, C. A. R., Halliday, D., and Harris, A. H. 1986. Factors causing development of resistance to phosphine by insect pests of stored produce. In: GASGA Seminar on Fumigation Technology in Developing Countries, Tropical Development and Research Institute, Slough, 141–149.

Fritz, G., Lorenz, K., Steinert, W., and Zellner, R. 1982. Laboratory kinetic investigations of the tropospheric oxidation of selected industrial emissions. In: Versino, B., and Ott, H., ed., Physico-chemical behaviour of atmospheric pollutants. Dordrecht, Reidel, 192–202.

Gras, P.W., and Bason, M.L. 1990. Biochemical effects of storage atmospheres on grain and grain quality. These proceedings.

Hah, J. K., Oh, J. W., Yoo, K. Y., and Kim, H. H. 1981. A study on gravity penetration of fumigants in the jumbo silo. Korean Journal of Plant Protection, 20, 103–106.

Harris, A. H. 1986. A conductimetric method for determining the concentration of phosphine during fumigation. In: GASGA Seminar on Fumigation Technology in Developing Countries, Tropical Development and Research Institute, Slough, 56–65.

Hole, B. D., Bell, G. H., Mills, K. A., and Goodship, G. 1976. The toxicity of phosphine to all developmental stages of thirteen species of stored product beetles. Journal of Stored Products Research, 12, 235–244.

Jay, E. 1980. Methods of applying carbon dioxide for insect control in stored grain. Advances in Agricultural Technology, Southern Series, S-13, U.S. Department of Agriculture.

Jay, E. G. 1986. Factors affecting the use of carbon dioxide for treating raw and processed agricultural products. In: GASGA Seminar on Fumigation Technology in Developing Countries, Tropical Development and Research Institute, Slough, 173–189.

Joubert, P.C., and du Toit, D. M. 1969. The development and yield of plants derived from fumigated seeds. I. Maize. Phytophylactica, 1, 195–200.

Kamel, A. H., Fam, E. Z., Maldi, M. T., and Sheltawy, E. M. 1974. The phytotoxic effect of carbon bisulphide, methyl bromide and hydrogen phosphide on the germination of seeds of certain field crops. Bulletin of the Entomological Society of Egypt, Economic Series, 8, 75–80.

Leong, E. C. W., and Ho, S. H. 1990. Susceptibility of *Liposcelis entomophilus* (Enderlain) to carbon dioxide. These proceedings.

Navarro, S. 1986. Gaseous fumigant mixtures, with special reference to mixtures of carbon dioxide. In: GASGA Seminar on Fumigation Technology in Developing Countries, Tropical Development and Research Institute, Slough, 150–158.

Navarro, S., Lider, O., and Gerson, U. 1985. Response of adults of the grain mite, *Acarus siro* L. to modified atmospheres. Journal of Agricultural Entomology, 2, 61–68.

Ohguchi, Y., Suzuki, H., Tatsuki, S., and Fukami, J. 1983. Lethal effect of oxygen absorber (Ageless) on several stored grain and clothes pest insects. Japanese Journal of Applied Entomology and Zoology, 27, 270–275.

Price, L. A., and Mills, K. A. 1988. The toxicity of phosphine to the immature stages of resistant and susceptible strains of some common stored product beetles, and implication for their control. Journal of Stored Products Research, 24, 51–59

Reichmuth, C. 1986. The significance of changing concentrations in toxicity of phosphine. In: GASGA Seminar on Fumigation Technology in Developing Countries, Tropical Development and Research Institute, Slough, 888–898.

Reichmuth, C. 1987. Low oxygen content to control stored product insects. Proceedings of the 4th International Working Conference on Stored-product Protection, Tel-Aviv, Israel, 194–207.

Ripp, B. E., Banks, H. J., Bond, E. J., Calverley, D. J., Jay, E. G., and Navarro, S., ed. 1984. Controlled atmosphere and fumigation in grain storages. Elsevier, Amsterdam. 798 p.

Shiroishi, M., Hayakawa, A., Okumura, K., and Umeda, K. 1961. Studies on methyl bromide. Journal of the Food Hygiene Society of Japan, 2, 47–53.

Taylor, R. W. D. 1975. The storage of seeds. Tropical Stored Products Information, 30, 23–33.

Taylor, R.W.D. 1975. The storage of seeds. Tropical Stored Products Information, 30, 23–33.

Tkachuk, R. 1972. Phosphorus residues in wheat due to phosphine fumigation. Cereal Chemistry, 49, 258–267.

Winks, R. G. 1986. The effect of phosphine on resistant insects. In: GASGA Seminar on Fumigation Technology in Developing Countries, Tropical Development and Research Institute, Slough, 105–118.

Winteringham, F. P. W., Harrison, A., Bridges, R. G., and Bridges, P. M. 1955. The fate of labelled insecticide residues in food products II. The fate of methyl bromide residues in wheat. Journal of the Science of Food and Agriculture, 6, 251–261.