Toxic Gas Treatment Responses of Insect Pests of Stored Products and Impact on the Environment

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Abstract

Both preventative and curative processes are used in integrated pest management of stored product pests. Use of toxic gases (fumigants) may be a final measure. The chemicals used must have particular qualities to make them suitable as fumigants, viz.:

- toxicity to the target pest
- high diffusion and penetration potential
- little reaction with treated produce
- harmless metabolites
- easy to handle
- easily detectable
- chemically unstable in the atmosphere
- harmless to the environment.

On the basis of this list, it is easy to conclude that only a few substances meet these requirements. Phosphine, methyl bromide, and hydrogen cyanide are the only fumigants remaining in widespread use in stored product pest control. The inert gases nitrogen and carbon dioxide are beginning to replace the toxic fumigants, particularly where storages to be treated are gastight or can economically be made so, and the length of the exposure period is not a limiting factor.

This paper discusses and compares the toxicity of these gases to various insects. Mode of action and occurrence of resistant strains are covered. Emphasis is placed on the environmental impact of these chemicals and possible risks to human health. New developments in fumigation techniques are discussed.

KEY activities in protecting stored products from insect pests are:

- creation of a pest and weatherproof enclosure for the product;
- monitoring the quality of the stored product, including detection of any pest infestation; and
- where pests are detected, employing appropriate methods of controlling their populations.

Commodities are sometimes disinfested before being placed in storage.

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The use of toxic gases, smokes, and vapours to control pests, especially insects, in stored agricultural products has a very long history. These chemical substances have a common ability to penetrate and distribute themselves through the products being treated.

Other types of chemicals, such as contact insecticides, have to be mechanically mixed with the product and their use is thus inconvenient or impractical. Moreover, treatment of products with residue-producing protectants before they are stored, although widely practiced is, for health and environmental reasons, becoming less acceptable to consumers.

Gases used as fumigants should have the following attributes:

- they are toxic to the target pests over short exposure periods
- they consist of small molecules with great potential to diffuse throughout the product to wherever pests may be located
- they leave insignificant or tolerable amounts of residues or metabolites in treated goods following ventilation
- they are easy to handle
- their presence is easy to detect, and concentrations can be readily monitored by fumigation personnel
- they are chemically unstable in the atmosphere after aeration
- they decompose into compounds harmless to the environment.

Gases meeting all these requirements are scarce and, due to the high standards of safety demanded, only a few chemicals are currently available for application as fumigants for pest control.

Hydrogen cyanide (HCN)

Hydrogen cyanide is renowned for its high toxicity, especially to mammals. It is still used for rodent control in ships, mills, and other food- and feed- processing factories. In the past, HCN has been used to treat citrus trees for control of scale insects and was also used for stored product insect pest control. However, the following serious disadvantages have led to preference being given to other compounds:

- high toxicity to humans
- high solubility in water, a problem in treatment of materials stored in damp cellars and of products with high moisture content
- arthropods displaying a protective stupefaction mechanism, which can result in their surviving treatment with the gas.

Peters and Ganter (1935) examined the mortality of adult *Sitophilus granarius* after treatment with HCN over a concentration range of 3.5–30 g/m^3 of HCN at temperatures of 17° and 35°C (Fig.1). The experiments included constant concentrations during treatment as well as variable concentrations, the latter, due to evaporation and diffusion (increasing concentration) and leakage and sorption (decreasing concentration), being characteristic of practical fumigations. Comparing all mortality results from the experiments with constant concentrations with those from varying concentrations showed clearly the applicability of Haber's rule to all dose mortality data.

Haber (1924; page 92) stated that for toxic gases the product of the amount of inhaled gas and the time during which an animal is inhaling the toxic air–gas mixture gives a good basis on which to assess the comparative toxicities of different fumigants. The rule itself states that, for a certain level of mortality, the product of the concentration and the exposure time is a constant. Peters and Ganter (1935) defined

$$W = C \times t \quad (1)$$

where W is the coefficient of efficacy (now known as the *Ct* product), c is the concentration of HCN in g/m^3, and t is the time in hours.

When plotting concentration versus time (Fig. 1), and marking the corresponding value that indicated 100% control and less than 100% control, they found that a hyperbola was formed between these two sets of points. At high temperatures the insects were more susceptible. The Ct product for complete kill at 35°C (between 20–30 $g.hours/m^3$), that at 25°C (about 60 $g.hours/m^3$), and that at 17°C (between 90 and 100 $g.hours/m^3$) showed a proportion of 1:2:3. Experiments at 0°C led, unexpectedly, to almost the same results as those at 17°C. Indeed, the *Ct* product was slightly reduced at 0°C. The possibility of protective stupefaction in this context was not deemed by Peters and Ganter to be sufficiently manifested. The cold as such did not have any pronounced influence, because weevils exposed at 0°C for 6 days without HCN were immobilised but showed no ill effects after removal from the low temperature. Experiments with changing concentrations had maxima of 12 g HCN/m^3 and 5 g HCN/m^3, respectively, and were combined with corresponding high or low concentration decay rates. Mortality rates closely approximated the *Ct* model when the integral of the concentration with time was used instead of the *Ct* product. The conclusion was, that Haber's rule described the dose–mortality relationship for adult *S. granarius* treated with HCN.

This result seems to contradict the results of Lindgren (1938), Pratt et al. (1931), and Gray and Kirkpatrick (1929). These authors described the occurrence of protective stupefaction for

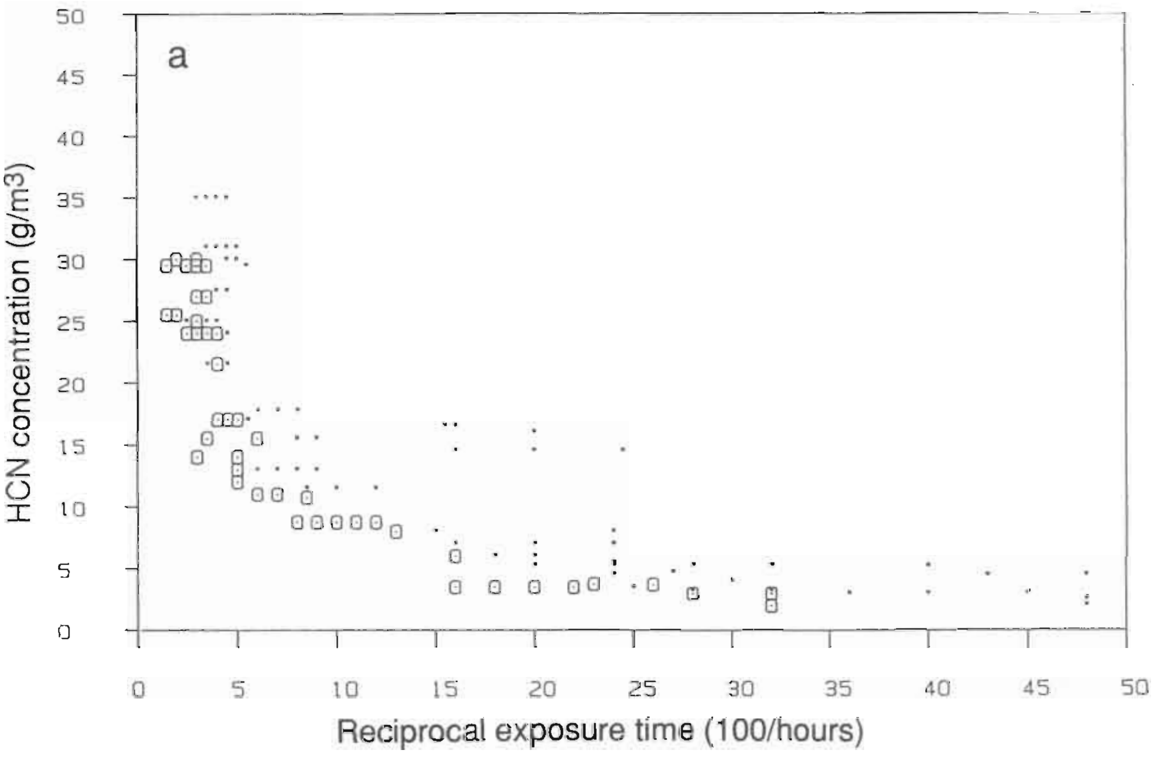


Fig. 1. Mortality of adult *Sitophilus granarius* after exposure to HCN at 17°C (• 100% mortality; ○ less than 100% mortality): (a – above) concentration of HCN in g/m^3 versus time in hours; (b – next page) concentration of HCN in g/m^3 versus reciprocal time in 100/hours (data of Peters and Ganter 1935).

As expected from Haber's rule a clear hyperbola can be drawn in Figure 1(a) between the two groups of data for 100% and less than 100% mortality.

Because the hyperbola can be given in the form

$Y = K \bullet 1/x$,

the inverse function must be a line:

$y = k \bullet z$; with $z = 1/x$ and the slope $s = k$.

Applied to the data of Peters and Ganter it follows that:

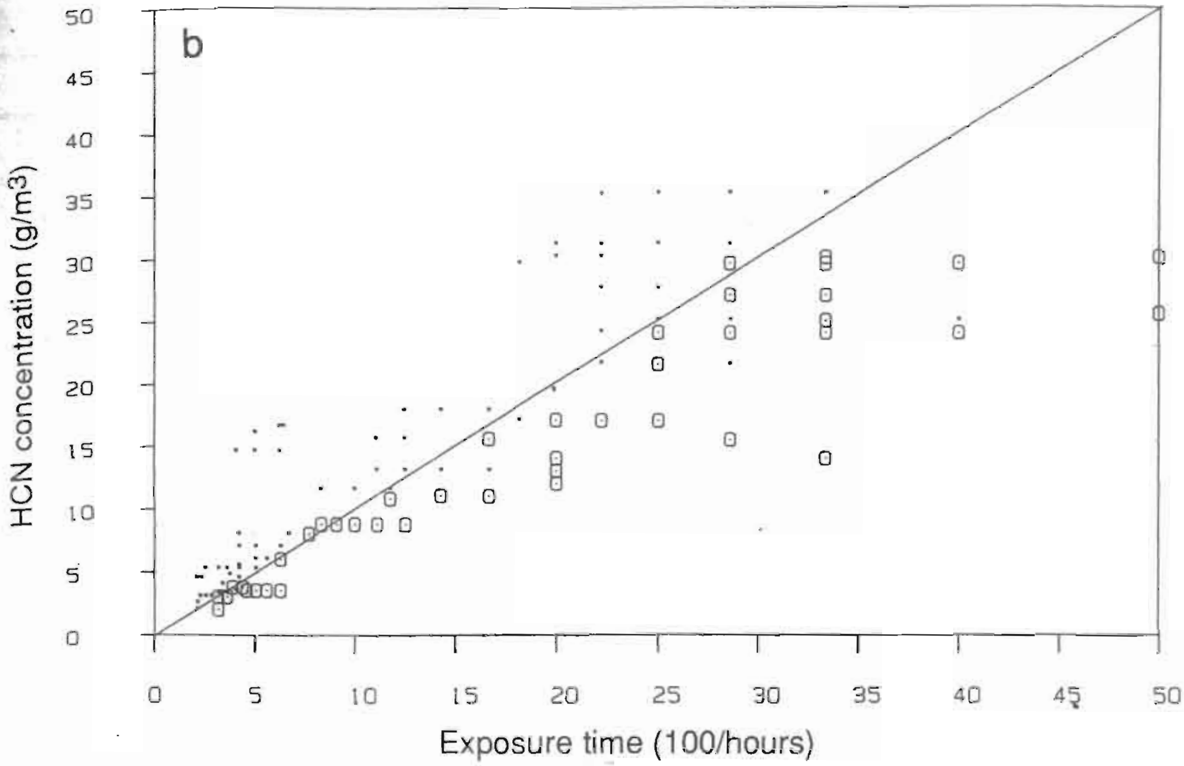
$C = k \bullet 1/t = k \bullet z$.

In Figure 1(b) the data are plotted in this reciprocal form. The result is a closely fitting line between the two groups of data. The line is extrapolated to facilitate calculation of its slope which contains the *Ct* product for 100% mortality. As can readily be seen the slope is unity, multiplied by 100, which is the transformation factor of the time axis. The slope *s* follows as:

$s = 100$ g.hours/m^3.

This is about the value of the Ct product derived by Peters and Ganter from their data.

some important arthropod pests including scale insects and *S. granarius*. The explanation is that the tolerance is increased when the insects are first stupefied with a fairly low dose approximately one hour before actual fumigation takes place. These parameters were used by Lindgren (1938), Pratt et al. (1931), and Gray and Kirkpatrick (1929), and were markedly different from the experimental conditions of Peters and Ganter. Bond (1963) described the important role of oxygen in the toxicity of hydrogen cyanide. Exclusion of oxygen from adult *S. granarius* prior to fumigation (48 hours fumigation to achieve LD_{50}, mortality count after 5 days, temperature not given) increased their susceptibility by a factor of 20. Price (1985, 1986b) discussed broadly the known facts and theories concerning the mode of action of fumigants. He suggested that the action of HCN is not merely a matter of respiratory inhibition, since the gas has an influence in the absence of oxygen.



Resistance to Hydrogen Cyanide

Resistance of insects to hydrogen cyanide has been discussed by Lindgren and Vincent (1965) and Bond (1984). The level of resistance reported is no more than a factor of 3. It should not be confused with protective stupefaction.

Methyl bromide

Haber's rule holds for methyl bromide over a wide range of temperatures, concentrations, and exposure periods. This, combined with the high specific toxicity, makes the gas a favourite candidate for pest control. It is relatively convenient and safe to handle. Limitations are:

- its boiling point of 4°C and condensation problems;
- a tendency to build up residues, especially in products with high fat content; and, last but not least,
- the suspicion that it is carcinogenic.

If the last limitation proves to be unfounded, methyl bromide will continue to be one of the most widely used fumigants. This seems unlikely, however, when all other halogenated hydrocarbon fumigants are currently banned because of health risks. It may remain useful and acceptable for disinfesting empty stores if the gas can be removed from the effluent air during ventilation after fumigation is complete.

In a recent paper, Bell (1988) gave the results of studies on minimum lethal concentrations of methyl bromide below which Haber's rule no longer applies. In the temperature range 15–25°C the efficacy threshold was found to lie between 0.5 and 4 g/m^3 for adults of 12 strains of stored-product beetles. At both temperatures, strains of *Tribolium castaneum* and *T. confusum* were more tolerant than strains of *Oryzaephilus surinamensis*, *Rhyzopertha dominica*, *Sitophilus granarius*, and *S. zeamais*. An increase in temperature from 15° to 20°C consistently almost doubled the efficacy threshold concentration levels. Bell indicated that further work is needed to determine minimum effective concentration levels. If flow-through methods for phosphine fumigation, such as those proposed by Winks (1986), are adapted to methyl bromide application it would be interesting to focus on the effective concentrations for 2–4 week exposures even though these concentrations lie outside the range of Haber's rule. Bell's work does not include methyl bromide concentrations of more than 4 g/m^3. Clearly, these concentrations have to be investigated, because of the variable concentrations characteristic of field fumigations (Fig. 1). For those concentrations above the efficacy threshold level, the mortality can be calculated by using the integral of the concentration versus time characteristic. However, the minimum lethal concentration, below which Haber's rule no longer applies, has to be determined in advance.

Howe and Hole (1966), working with *Sitophilus granarius,* found the early pupa to be the developmental stage of this species most tolerant to methyl bromide at 25°C, using concentrations of 3–9 g/m^3. It was estimated that *Ct* products of more than 50 g.hours/m^3 were needed to kill 99.9% of a population of *S. granarius* at 25°C. Fumigation leads to delay in emergence. Fortunately, if the lethal response to methyl bromide fumigation is extrapolated from experiments with low concentrations to those with high concentrations the amount of gas actually needed is less than calculated. The corresponding probit lines are curved, leading to overestimation of the dose required (Howe and Hole 1967). Thus, 52.5 g.hours/m^3 (10 g/m^3) gave total kill of developing *S. granarius* at 25°C, in contrast to the 75 g.hours/m^3 estimated. Furthermore, the survivors of sublethal treatments were short-lived and infertile when the dose was close to 100% effective.

Since gas is always lost by leakage and/or absorption by the product treated, the dosage must be increased to allow for these losses. Because it is possible to meter gas concentration during a fumigation, it is feasible to add fumigant if low values are found (Howe and Hole 1967). In addition, a check for gastightness should be part of the pre-fumigation routine.

Resistance to Methyl Bromide

Using a methyl bromide concentration of 4 g/m^3, Hole (1981) found many field strains of stored product Coleoptera from all over the world to be about twice as tolerant as laboratory strains. This is in accordance with results of the FAO survey by Champ and Dyte (1976), and of Monro and Upitis (1956) who selected for resistance in the laboratory. Monro et al. (1961) subsequently reported that this artificially induced tolerance was retained for at least 23 generations after cessation of exposure to the fumigant and so could be defined as resistance. This high tolerance could be transferred to hybrids by crossing resistant and susceptible strains.

Phosphine

Phosphine is currently the most widely used fumigant in stored product protection. Its chemical properties and use are described elsewhere (Fluck 1973; Bond 1984; Reichmuth 1988). Phosphine fulfills many of the requirements of a fumigant for pest control, but has some disadvantages, viz:

- exposure times are relatively long
- it has a high specific toxicity for mammals
- it corrodes various metals
- high levels of resistance are prevalent due to poor fumigation practices.

Phosphine's advantages explain its widespread use:

- formulations of metal phosphides are safe and easy to handle
- the gas may be associated with a strong warning smell (sometimes masked!)
- it is efficacious at very low concentrations
- it leaves low levels of residues
- it is metabolised rapidly, leaving harmless metabolites
- if properly applied, it has no deleterious effect on the environment.

Bell et al. (1985) gave the following *Ct* products for 100% kill of *Trogoderma granarium* including the very tolerant diapausing larvae and young eggs: 75 g.hours/m^3 (8 days exposure), 100–200 g.hours/m^3 (6 days exposure) at 15°C ; 0.7–1.4 g.hours/m^3 at 20 °C; and 45 g.hours/m^3 for 2 days exposure at 25°C. Winks (1982, 1984, 1986) exhaustively investigated the toxicity of phosphine to adults of *Tribolium castaneum* at 25°C and 70% R.H. A *Ct* relationship:

$$C^{0.9} \bullet t = W \qquad (2)$$

provided a good description of toxicity. The beetles became narcotised and were partially protected from the effects of phosphine at concentrations greater than 0.5 mg.hours/L. Narcosis was defined as a state of immobility.*

Reichmuth (1985) compared the *Ct* products required to achieve a specified mortality of

*In populations exposed to concentrations producing narcosis, it is the insects that are not immobilised that are likely to survive. Narcotised insects usually succumb. Eds.

adult *S. granarius* after exposure to constant concentrations with those of exposure to increasing and decreasing concentrations. With phosphine, in contrast to hydrogen cyanide (Peters and Ganter 1935), Haber's rule did not apply to both types of experimental conditions (Figs 2 and 3). The values of the integrals over concentration/time curves leading to the same mortality were much greater in the case of changing compared with fixed concentrations. The difference was by a factor of about 20. The same difference in response applied also to immature stages of *S. granarius* (Reichmuth 1986). In general terms it can be concluded that increasing the concentration of phosphine does not increase the mortality by nearly as much as would be expected. This has often been observed (e.g. Bell 1986). Equation (2), given earlier and used by Winks (1984, 1986), shows clearly that exposure time is the more important parameter in achieving a specified insect mortality. In logarithmic scales for both axes, the influence of the exponent can be judged from the slope of the graph log t versus C (Winks 1984):

$$\log t = -W - 0.9 \log C \text{ (i.e. slope} = -0.9\text{)} \quad (3)$$

Increasing steepness of the slope of the graph expresses growing influence of the exposure period. Equation (3) applies only to the linear part of the probit plane and not to the concentration/time area, which is defined to be 'the narcotic region' (Winks 1984) (Fig. 4). As already indicated, this deviation should not be considered as 'protective stupefaction' which involves pretreatment before the actual exposure.

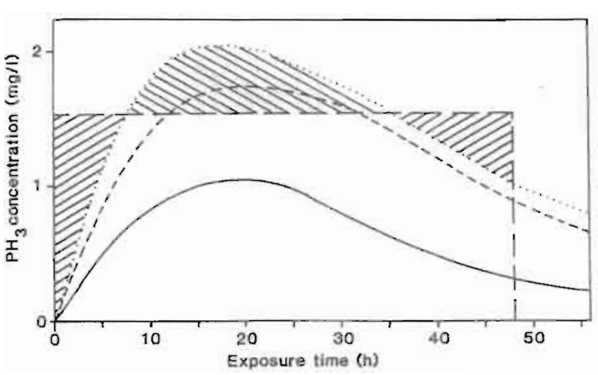


Fig. 2. Gas concentration characteristics of phosphine fumigations with adult *Sitophilus granarius* following an initial dosage of 6 (..........), 4 (– – –), and 2 (——) g/m^3 of phosphine at 20°C, 76% RH, and a leakage rate of 5% of the volume of the treated enclosure per hour. The two shaded areas of the rectangle are equivalent to the shaded area under the dotted curve, so that the rectangle corresponds to the integral of the dotted curve.

Resistance to Phosphine

It is clear that immobilised insects continue to take up phosphine. With adult *Tribolium castaneum* it was shown that resistant insects took up phosphine at a lower rate than susceptibles. This was investigated in vivo using radiolabelled phosphine (Figs 5 and 6). The amount of phosphine that needed to be incorporated to kill resistant insects was greater than the corresponding amount for susceptible insects. The

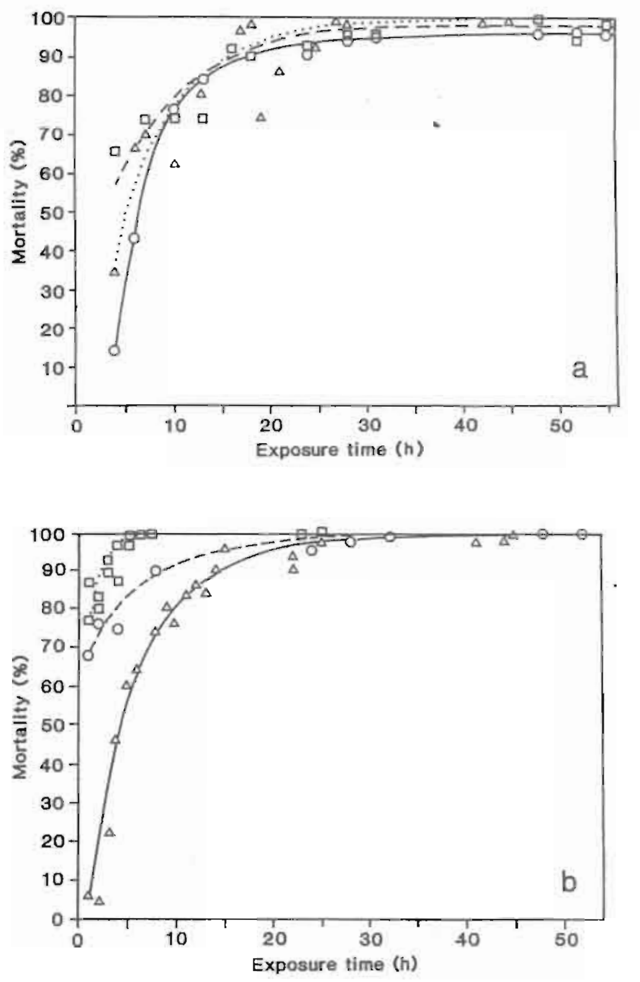


Fig. 3. (a) Mortality results from phosphine treatment of adult *Sitophilus granarius* with 6 (Δ), 4 (□), and 2 (○) g/m^3 aluminium phosphide formulation at 20°C, 75% RH, and a leakage rate of 5% of the volume of the treated enclosure per hour.
(b) Mortality results from phosphine treatment of adult *Sitophilus granarius* with at 1.55 g/m^3 (□), 0.90 g/m^3 (○), and 0.08 g/m^3 (Δ)at 20°C and 75% RH.

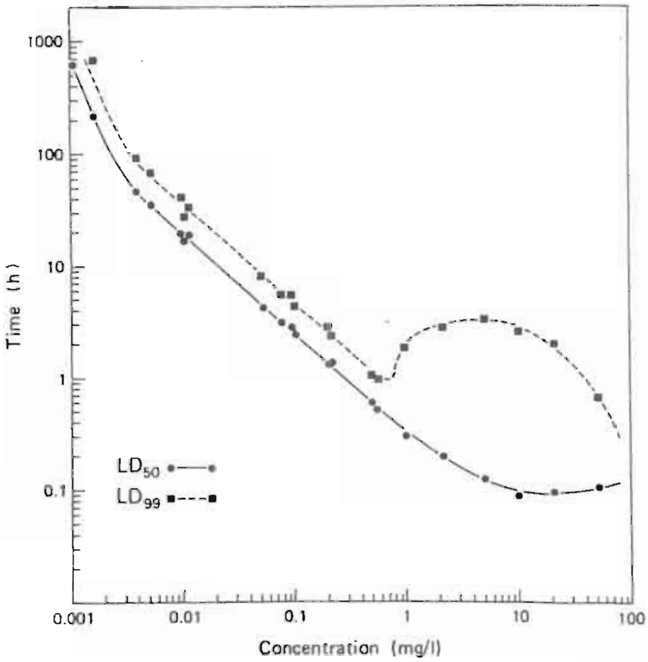


Fig. 4. The concentration × time relationship at the LD_{50} and LD_{99} levels for *Tribolium castaneum* adults exposed to a range of fixed concentrations for various exposure periods (data of Winks 1984). The data for LD_{99} indicate very clearly that, for concentrations of phosphine above 0.7 g/m^3, Haber's rule does not apply in this so-called narcotic range. Moreover, increasing concentration beyond 0.7 g/m^3 requires an *increase* in exposure time to achieve the same mortality as at lower concentrations. This agrees with the finding of Reichmuth (1985) that steadily increasing concentrations of phosphine gradually became less effective against *S. granarius*.

reduced uptake by resistant insects is in accordance with findings of Price (1985), who suggested that active exclusion is a characteristic of phosphine resistant strains of *Rhyzopertha dominica*. One of the clear findings of studies using radiolabelled phosphine was that those insects that tend to stay active for the longest time (i.e. those not narcotised) are those that will most probably survive. This is especially true with resistant adult beetles and was observed during the experiments. The same phenomenon is described by Price (1986a).

New Aspects of Phosphine Fumigation

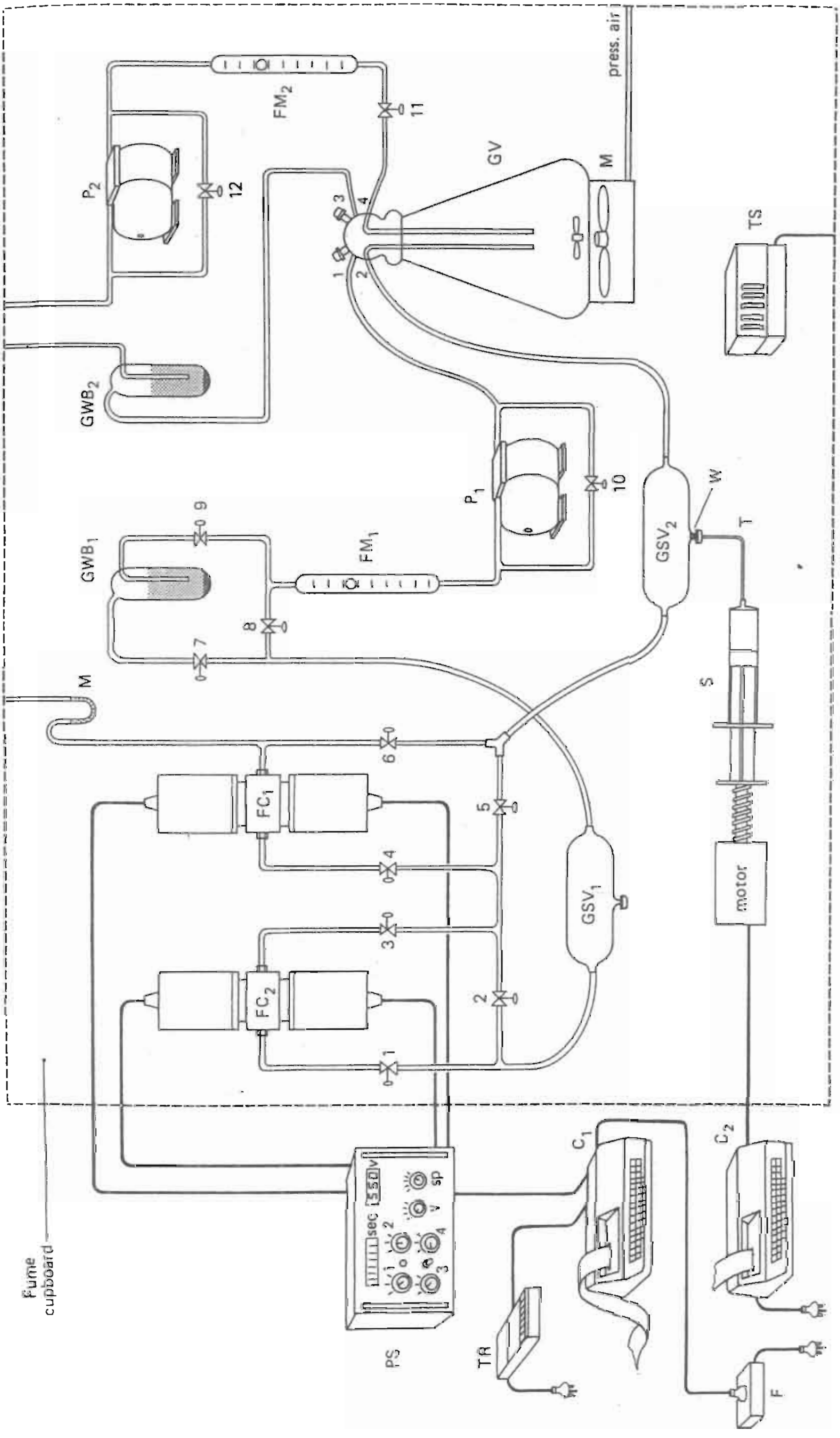
For fumigation during cold weather, Sullivan (1985) proposed use of magnesium phosphide rather than aluminium phosphide because of more rapid evolution phosphine from the magnesium formulation at low temperatures. Insect control data were not given. Cook (1980), Reichmuth (1985), Sullivan (1985), Banks (1986), Winks (1986), and Wohlgemuth (1986) all dealt with the question of recirculating the gas through bulk grain or using a flow-through method. The great advantage of these techniques is that the stored product need not be turned to add the formulation. Uniform distribution of the gas is easily achievable given a specified degree of gastightness. In the case of flow-through techniques, exposure time must be some weeks to ensure complete kill at low concentrations. In any case, because time of exposure is the governing factor in phosphine toxicity, long exposure periods are preferable to minimise the dosage. Moreover, concentration needs to be low to avoid environmental risks. A further development might be the sorption of the gas in some way as it is purged from the bulk rather than venting it to the air. These ideas are stimulated by the increasingly stringent regulations on fumigation being imposed in the Federal Republic of Germany.

Controlled Atmospheres

Due to growing concern on the use of toxic materials, gases such as nitrogen and carbon dioxide have come back into focus for stored product pest control. Annis (1987) surveyed insect pest control with these fumigants at temperatures above 20°C. Reichmuth (1987) did likewise for the temperature range 15°–20°C. Lethal exposure times for immature *S. granarius* are shown in Table 1. At 15°C, older larvae and pupae had to be exposed to high nitrogen atmospheres for about 60 days for 95% mortality, a less effective regime than 16–19% CO2. In high carbon dioxide atmospheres, only 35–40 days were necessary for complete control. At 20°C these times were reduced to 30–40 days and to 25–38 days, respectively.

The future potential of these gases as 'Controlled Atmospheres' (CA) is strongly dependent on the level of gastightness of the treated premises. Love et al. (1983) have given figures that indicate the economic range for their use when warehouses are made gastight and used over a period of years.

Generally speaking, exposure time is not a limiting factor with CAs. At 30°C a few days are sufficient, at 20°C a week or two, and at 15°C about a month is needed to control various species of stored product pests, with pupae of *S. granarius* being most tolerant. Normally, one


press. air
FM2
GV
M
P2
TS
GWB2
P1
W
T
GSV2
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motor
GSV1
FC2
C1
C2
Fume cupboard
PS
TR
F

purge of the whole volume is necessary to remove the air from the product. The purge rate during the exposure period depends on the gastightness, although in some cases only an initial purge is necessary, making CA-application very economic.

Since the gases are costed by weight, it is worth noting that 1 kg of liquefied nitrogen produces 1 m^3 of gas, while 1 kg CO_2 yields only 0.5 m^3 of gas. This fact—along with other parameters such toxicity, availability, safety, sorption, and quality of treated product—may influence the choice of the gas. With nitrogen the oxygen concentration must be depressed below about 4% by volume, while carbon dioxide is lethal below an oxygen content of about 6% by volume. Insects, like mammals, are rapidly narcotised by carbon dioxide at low oxygen contents and low levels of resistance to carbon dioxide, established by selection in the laboratory, have been reported. Bond and Buckland (1979) found tolerance factors between 1.8 (LT_{99}, 4 generations at 75% CO_2) and 3.3 (LT_{99}, 7 generations at 42% CO_2) with adult *S. granarius,* and Navarro et al. (1985) determined factors of 2.2 (LT_{95}, 7 generations at 40% CO_2) and 3.3 (LT_{95}, 10 generations at 75% CO_2) with *S. oryzae.*

The use of pressurised CO_2 in high-pressure chambers was recently demonstrated for insect control (Gerard et al. 1988) (Figs 7 and 8). This costly method has only a limited market for treating high-value products such as drugs, tea, and cocoa, its advantage being that only short exposure periods — of the order of hours — are needed.

Environmental and Health Aspects of Fumigation in Stored Products Protection

Some 10 years ago Reichmuth et al. (1981) began a project to assess the likely risks of the application and emission of fumigants used in stored product protection. Measurements in and around fumigated structures such as flour mills, warehouses, and granaries led to the conclusion that only within 10 m of such facilities would values of more than 0.15 mg/m^3 of phosphine (the German TLV) be detectable on a regular basis (Reichmuth and Noack 1983). In the event of an accident, higher concentrations might occur at greater distance from a structure being fumigated, but only for a very short period. This study involved large granaries, warehouses, and mills with an average level of sealing quality. The results for methyl bromide and HCN were very similar. The German TLVs were very rarely exceeded at distances more than 10 m from the structure. These results con-

Fig. 5 (previous page). Diagram of apparatus for monitoring phosphine uptake by insects at constant or varying concentrations.

FC_1 and FC_2 are fumigation chambers (≈ 100 mL) and FC_1 contains the insects; power supply (PS) and counting device (Computer C_1) for the Geiger tubes; the voltage of the Geiger tube (550 V) can be adjusted with switch V for the four tubes 1, 2, 3, and 4; the time relative to the beginning of the experiment is indicated in seconds or minutes; this can be selected with the switch between voltage potentiometer 3 and 4; time reset button between voltage potentiometer 1 and 2; select switch SP for a loudspeaker to indicate acoustically radioactivity at the four Geiger tubes, fifth position is off-position; filter F saves the computer from spikes derived from the main voltage supply; pump P1 circulates the gas; flow adjustment at tube clamp 10, flow indication at flowmeter FM_1, humidification of the gas in a gas-washing bottle GWB_1 which contains a saturated NaCl solution and some residual NaCl salt at the bottom, regulation with clamps 7, 8, and 9; monitoring of the gas concentration at gas sampling vessel GSV_1 with syringe through the septum of this vessel, clamps 1 to 6 determine the actual flow path of the gas, manometer M shows the pressure in the system; a septum in gas sampling bottle GSV_2 can be used to introduce gas slowly from a syringe S, the plunger being driven by a motor according to a gas release characteristic which can be programmed into Computer C_2, the tip of the syringe inside GSV_2 is covered with water W to avoid free diffusion from the tip, the gas in the gas mixing vessel GV containing 2 septum ports for injection or withdrawing of gas is stirred by a magnet which is driven by another magnet outside on top of a rotor M being driven by pressurised air; for simulation of leakage port 3 and 4 of GV can be used to withdraw gas with pump P_2, regulated with clamp 12, the flow is indicated at flowmeter FM_2; the withdrawn gas is continuously replaced by fresh humidified air (gas washing bottle GWB2); the temperature of the installation is regulated constantly to 25 ± 0.3°C using a thermosensor TS which is placed close to the apparatus inside a fume cupboard which is sucking continuously air outside the laboratory because of safety reasons; the leads of the electrical equipment are led through holes in the walls of the cupboard.

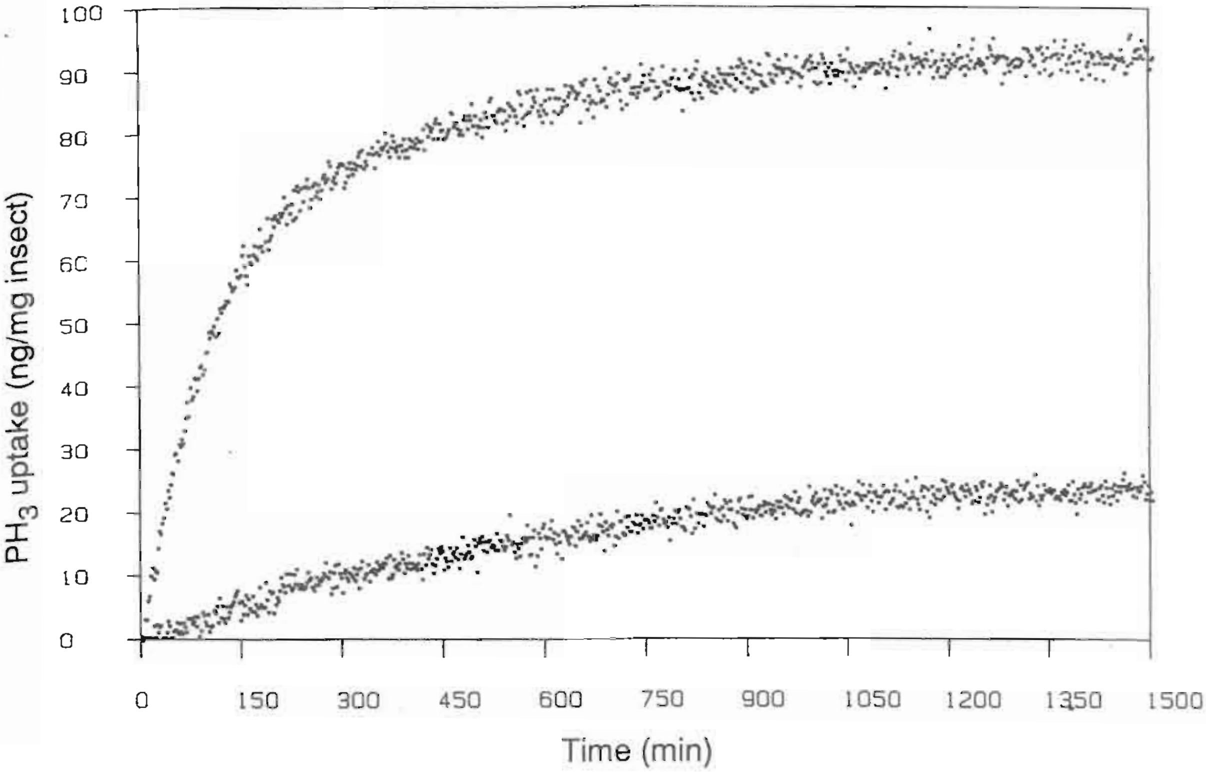

Fig. 6. Phosphine uptake by 10 resistant (IR) and 10 susceptible (II S) adults of *Tribolium castaneum* during exposure to 1 g/m³ phosphine at 25°C. The change in uptake rate (flattening of the curves) is correlated to mortality of the insects. The horizontal parts of the lines indicate uptake by moribund or dead insects.

firmed those of Arendt et al. (1979). Meanwhile, due to changing public health consciousness in the FRG, stimulated by environmental accidents involving chemicals, a concentration level of 1/5 of the German TLV (0.02 ppm v/v) has been declared the critical level. This value must not be exceeded during a fumigation at places where people live. The fumigator-in-charge has to measure and make sure that no persons are exposed to higher concentrations. If needs be, he must evacuate the the area (at the cost of the fumigation firm) to ensure that young children, and ill, elderly, or other sensitive persons are not placed at risk.

In the course of the study, the possibility of

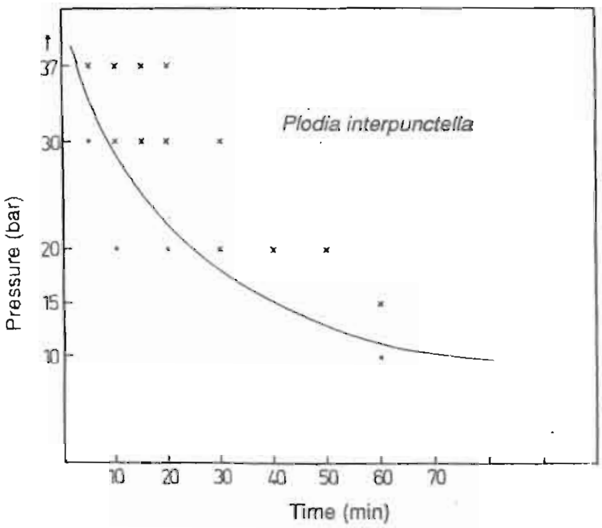

Fig. 7. Survival (•) and 100% mortality (x) of eggs of *Plodia interpunctella* after exposure to high pressure and carbon dioxide. At room temperature good results can be achieved in less than 1 hour.

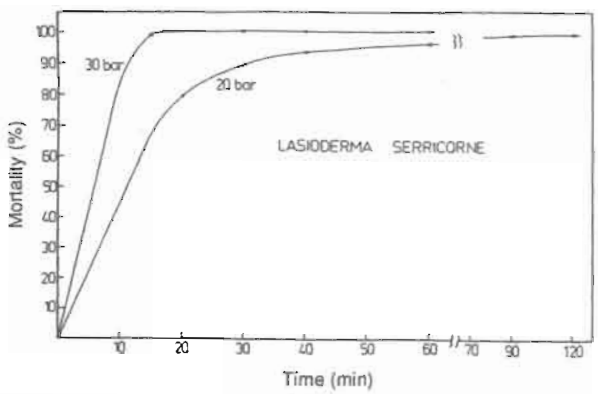

Fig. 8. Response of adult and immature *Lasioderma serricorne* to high pressure and carbon dioxide at room temperature.

Table 1. Lethal exposure time (LT95) in days for immature *Sitophilus granarius* exposed to varying concentrations of nitrogen and carbon dioxide at 15°C and 20°C and oxygen contents of 1–4% by volume. B1 ... B5: 3 day age cohorts* of various developmental stages cultured at 70% RH and 25°C.

Oxygen content (vol %)	Gas mixture	Lethal exposure times (days) 15°C B1	B2	B3	B4	B5	20°C B1	B2	B3	B4	B5
		(Age cohorts)					(Age cohorts)				
$1\%\ O_2$	$+99\%\ N_2$	30	40	40	40	45	20	13	21	30	30
	$+80\%\ N_2$ $+19\%\ CO_2$	30	35	45	60	39	16	27	29	30	32
	$+4\%\ N_2$ $+95\%\ CO_2$	30	9	15	22	35	16	2	11	20	24
$2\%\ O_2$	$+98\%\ N_2$	30	40	40	60	52	12	13	25	31	25
	$+80\%\ N_2$ $+18\%\ CO_2$	20	35	35	53	49	14	14	14	25	21
	$+8\%\ N_2$ $+90\%\ CO_2$	13	12	25	15	27	10	5	5	7	19
$3\%\ O_2$	$+97\%\ N_2$	30	31	45	65	53	17	12	28	35	30
	$+80\%\ N_2$ $+17\%\ CO_2$	32	33	40	50	41	15	18	25	42	45
	$+12\%\ N_2$ $+85\%\ CO_2$	21	11	9	24	34	10	2	9	15	26
$4\%\ O_2$	$+96\%\ N_2$	40	25	60	60	55	32	18	25	40	40
	$+80\%\ N_2$ $+16\%\ CO_2$	46	32	40	48	49	18	7	18	31	32
	$+16\%\ N_2$ $+80\%\ CO_2$	45	15	31	39	40	23	18	25	40	38

* Age cohorts are: B1, eggs, 0–3 d old; B2, larvae, 7–10 d old; B3, larvae, 14–17 d old; B4, pupae and larvae, 21–24 d old; B5, pupae, 28–31 d old.

harmful effects of low concentrations on plants and animals was also investigated (Noack and Reichmuth 1981, 1982). It was found that 0.1 ppm v/v phosphine in air is about the limit value for significant damage to *Drosophila melanogaster*, which is classed as a very susceptible animal. The threshold concentration of phosphine in air for harmful effects on growing lettuce (a highly sensitive plant species) was determined to be between 3 and 8 mg/m^3 (20 and 53 ppm v/v). In another experiment, a common ornamental plant (*Diefenbachia*) was unharmed by exposure to 10 ppm v/v phosphine for 14 days at room temperature (22°C) and 80-90% RH.

The concentration limit below which there will be no harm to exposed persons is problematic. The issue is discussed in general terms by Jackson et al. (1988). Klimmer (1969) found that 1.4 and 3.5 mg/m^3 of phosphine applied for 4–6 hours per day, for 6 days a week, for a total of more than 800 hours over a 24-week period produced no clinical, laboratory, or pathological evidence of effects on exposed cats, guinea-pigs, and rats. Pazynich et al. (1984) exposed white rats to 0.05, 0.2, 1.5, and 8 mg/m^3 of phosphine. Changes in blood cholinesterase, peroxidase, and catalase activity and in phagocyte behaviour were found. They were not generally dose-related. The authors recommended mean exposure limits for urban air, for exposure durations of 24 hours, one month, and one year of 0.004, 0.0015, and 0.001 mg/m^3 phosphine, respectively, with a ceiling value of 0.01 mg/m^3. This recommendation has been adopted in the USSR. In a similar study, Atchbarov et al. (1984) found significant medical changes in rats inhaling 0.1 and 0.05 mg/m^3 phosphine.

From the available literature on human toxicity (e.g. Waritz and Brown 1975; Amoore and Hautala 1983; Jackson et al. 1988) the conclusion can be drawn that very low concentrations of phosphine inhaled over periods of several hours or days might have minimal toxic effects. In practice, the periods of exposure are very short and sporadic for fumigation personnel and for persons close to a facility being fumigated and therefore not critical when gas concentrations are regularly checked and gas masks are at hand in case of complications. Serious accidents have occurred only when persons slept immediately outside a treated premises — which is strictly forbidden — or where safety precautions were not taken. It must be added that during certain weather conditions (e.g. inversions) gas might diffuse from the premises and drift away without turbulent mixing. On these rare occasions care must be taken to check gas concentrations at greater than usual distances from the fumigated premises.

Due to these uncertainties surrounding granary fumigation it is suggested that the emission of gas might be prevented by continuously sucking the free air out of the treated premises and purging it through a sorbing unit. The gas which is diffusing through the plastic cover of the grain into the airspace is thus continuously removed. During the period of aeration the same principle could be used. Using this strategy, only minute amounts of the gas would escape into the environment.

Fritz et al. (1982) investigated the stability of phosphine in the atmosphere and found a median lifespan of less than one day: conversion to hypophosphoric acid was suggested. Experiments to determine the rate of hydrolysis of methyl bromide showed that light enhances it markedly (Castro and Belser 1981). From these results it can be concluded that the stability of methyl bromide in the atmosphere is of the order of days or less. On the other hand, Singh (1988) reported the occurrence of methyl bromide in stratospheric air but not (yet) in the stratosphere of middle or lower latitudes. This methyl bromide might originate from the catalytic destruction of ozone by ClO_x and BrO_x radicals.

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