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Fumigation for Soil Pest Control

Fumigation continues to play a valuable role in many pest control operations; however, both the concepts and the procedures for controlling insects and other organisms are changing. With increased public concern over the adverse effects of pesticidal chemicals on human health and the environment, greater emphasis is being given to methods that can circumvent the use of these materials. Nevertheless, the need for chemical pesticides, particularly the fumigants, is likely to continue for many years to come; fumigants have unique properties and capabilities that permit use in numerous situations where other forms of control are not feasible or practical.

Fumigants are a unique and particularly valuable group of pesticides that can kill insects where no other form of control is feasible. To a large extent they are irreplaceable. The use of certain fumigants has been restricted in some countries because of suspected adverse effects. Excessive use of fumigants or the misuse of them to cause accidents and produce adverse publicity is likely to bring about even greater restrictions in their use. By careful planning and management, fumigation may be incorporated into food preservation systems so that fumigants can be used more effectively and safely than when used independently. They should never be used as a substitute for sound management and good sanitation procedures. The benefits derived can include reduced cost of storage with improved food quality, reduced residues in food materials, greater occupational safety and less environmental contamination. All of these benefits are of great concern to the general public and will be factors that have to be taken into consideration in the future use of fumigants. The ultimate goal in the control of pests in stored products should be to so improve the methods of handling, storing and processing commodities, that the need for pesticides will decrease. Fumigants will then only be needed when unavoidable infestations are encountered.

CHOICE OF FUMIGANT

There are many chemical compounds which are volatile at ordinary temperatures and sufficiently toxic to fall within the defintion of fumigants. In actual practice, however, most gases have been eliminated owing to unfavourable properties, the most important being chemical instability and destructive effects on materials. Damage to materials may take place in several ways, as follows:

1. Excessively corrosive compounds attack shipping containers or spoil the structure and fittings of fumigation chambers or other spaces undergoing treatment.
2. Reactive chemicals form irreversible compounds, which remain as undesirable residues in products. In foodstuffs such reactions may lead to taint or the formation of poisonous residues. Other materials may be rendered unfit by visible staining or by the production of unpleasant odours.
3. Physiologically active compounds may destroy or severely injure growing plants, fruit or vegetables, and may adversely affect seed germination.

Highly flammable compounds are not necessarily excluded if dangers of fire and explosion can be controlled by the addition of other suitable compounds, or if fumigation procedures are carefully designed to eliminate these hazards. Toxicity to human beings is not necessarily a cause for exclusion. All known fumigants are toxic to humans to a greater or lesser degree and ways can be devised for their safe handling under the required conditions of application. However, some commonly used compounds have been shown to be capable of producing long-term effects that were previously unknown. The use of such fumigants is becoming more restricted and some materials have already been eliminated from the list of fumigants approved for use in certain countries.

EVAPORATION OF FUMIGANTS

Boiling Point

The boiling point of different chemical compounds generally rises with the increase of molecular weights. If the highest possible concentrations are required at the beginning of the fumigation with such compounds, more rapid volatilsation will have to be effected in some way.

From the physical standpoint, fumigants may be divided into two main groups according to whether they boil above or below room or moderate outdoor temperatures (20°C to 25°C). The low boiling point fumigants, such as methyl bromide, may be referred to as gaseous -type fumigants. These are kept in cylinders or cans designed to withstand the pressure exerted by the gas at the highest indoor or outdoor temperatures likely to be encountered. The second main group of fumigants contains those with high boiling points; these are usually described as liquid-type or solidtype according to the form in which they are shipped and handled. In some kinds of work, such as grain and soil fumigation, the slow evaporation of certain liquids is an advantage because the initial flow leads to a better distribution of the gas subsequently volatilsed. In other applications, where personnel have to distribute the fumigants, slow evaporation of the liquids or solids makes them safer to handle.

Included in the general term solid-type fumigants are certain materials which are not fumigants themselves, but which react to form fumigants after application. Examples are calcium cyanide powder, which reacts with atmospheric moisture to yield hydrogen cyanide (HCN), and formulations of aluminium and magnesium phosphides which also react with moisture to produce phosphine (hydrogen phosphide).

There are also some fumigants in the form of crystals and flakes that sublime to give off fumigant vapours. Examples are paradichlorobenzene and naphthalene.

Maximum Concentrations

The maximum weight of a chemical that can exist as a gas in a given space is dependent on the molecular weight of that chemical. This fact, implicit in the well-known hypothesis of Avogadro, has an important practical application. It is useless attempting to volatilise in an empty chamber more fumigant than can exist in the vapour form.

Commodities treated and remarks

Tobacco and plant products; also spot treatment. Injures growing plants, fresh fruit and vegetables. Marketed with carbon tetrachloride.

Grain. Usually as ingredient of nonflammable mixtures. Only weakly insecticidal. Used chiefly in mixture with flammable compounds in grain fumigation to reduce fire hazard and aid distribution.

Grains and plant products. Injurious to living plants, fruit and vegetables. Highly irritating lachrymator. Bactericidal and fungicidal.

Insects in open space of structures. Does not penetrate commodities.

General fumigant. Particularly useful for certain fruit; may injure growing plants.

Seeds and grains. Usually mixed with carbon tetrachloride.

Grains, cereals and certain plant products. Toxic at practical concentrations to many bacteria, fungi and viruses. Strongly phytotoxic and affects seed germination.

Application to individual packages of dried fruit.

General fumigant, but may be phytotoxic. Safe on seeds but not recommended for fresh fruit and vegetables.

General fumigant. May be used with caution for nursery stock, growing plants, some fruit and seeds of low moisture content.

Usually mixed with CO_2. Formerly used for grain, now mainly for stored furs.

Control borers in peach trees and soil insects. Applied as crystals. May affect seed germination.

Grain and processed food fumigant; gas generated from aluminium or magnesium phosphide.

Control of dry-wood termites in structures.

Nonflammable ingredient of grain fumigants. Sometimes used alone.

Latent Heat of Vaporisation

Unless it is sustained by warming from an outside source, the temperature of an evaporating liquid constantly drops owing to the fall in energy caused by the escape of molecules with greater than average energy. Thus, evaporation takes place at the expense of the total heat energy of the liquid. The number of calories lost in the formation of one gramme of vapour is called the latent heat of vaporisation of the liquid. Some fumigants have higher latent heats than others.

Both HEN and ethylene oxide, with latent heats of 210 and 139 respectively, absorb considerably more heat in passing from liquid to than do methyl bromide and ethylene dibromide, with latent heats of 61 and 46 respectively.

The factor of latent heat is of important practical significance. The high pressure fumigants, such as HCN, ethylene oxide and methyl bromide, are usually kept under pressure in suitable cylinders or cans. On release into the atmosphere, volatilisation takes place rapidly and, unless the lost heat is restored, the temperature of the fumigant may fall below the boiling point and gas may cease to be evolved. Also, as the liquid changing to gas is led through metal pipes and tubes, or rubber tubing, the fall in temperature may freeze the fumigant in the lines and prevent its further passage. In many applications, to be described elsewhere in this manual, it is advisable to apply heat to the fumigant as it passes from the container into the fumigation space.

Fumigants that are liquids at normal temperatures and are volatilised from evaporating pans or vaporising nozzles may require a source of heat, such as a hot plate, in order that full concentrations may be achieved rapidly.

Diffusion and Penetration

Fumigants are used because they can form insecticidal concentrations: (a) within open structures or (b) inside commodities and in cracks and crevices into which other insecticides penetrate with difficulty or not at all. Hence, it is necessary to study the factors that influence the diffusion of gases in every part of a fumigation system. This study includes the behaviour of fumigants both in empty spaces and also in structures loaded with materials into which the gas is required to penetrate.

Law of diffusion

Graham's law of diffusion of gases states that the velocity of diffusion of a gas is inversely proportional to the square root of its density. Also, the densities of gases are proportional to their molecular weights. Therefore, a heavier gas, such as ethylene dibromide, will diffuse more slowly throughout an open space than a lighter one such as ethylene oxide. While this basic law is of importance, especially for empty space fumigations, the movement of gases in contact with any internal surface of the structure or within any contained materials is greatly modified by the factor of sorption discussed below. The rate of diffusion is also directly related to temperature, so that a given gas will diffuse more quickly in hot air than in cold air.

Specific gravity and distribution

Many of the commonly used fumigants are heavier than air. A notable exception is hydrogen cyanide. If a gas heavier than air is introduced into a chamber filled with air and it is not agitated by fans or other means, it will sink to the bottom and form a layer below the air. The rate of mixing between the two layers may be very slow. For example, in a fumigation of the empty hold of a ship with the heavy gas methyl bromide where the fumigator had neglected to place a circulating fan, a sharp demarcation was observed between the lower half with the gas, where all of the insects were killed, and the upper part, where complete survival occurred.

In good fumigation practice, settling or stratification will not be encountered if adequate provision is made to disperse the gas properly from the very beginning of the treatment. Even distribution can be ensured by employing singly or in suitable combination:multiple gas inlets, fans or blowers and/or circulation by means of ducts and pipes. Contrary to popular belief, once a gas or number of gases heavier than air have been thoroughly mixed with the air in a space, settling out or stratification of the heavier components takes place very slowly; so slowly, in fact, that once a proper mixture with air has been secured, the problem of stratification of a heavierthan-air fumigant is of no practical importance for the exposure periods commonly used in fumigation work.

Mechanical aids to diffusion

It has already been suggested that distribution and penetration can be aided and hastened by the use of blowers and fans. Such propellers may work free in the structure or through a system of circulating ducts. These devices may also add greatly to the efficiency of the fumigation process by hastening the volatilisation of high boiling point liquids from evaporating pans and by preventing stratification of heavy gases. Also, a factor known as the Turtle effect* has proved useful in the fumigation of certain materials susceptible to injury. It was shown that rapid stirring by a centrifugal fan in a fumigation chamber at atmospheric pressure greatly hastened the attainment of uniform concentrations of methyl bromide in all parts of a load of early potatoes, so that the consignment was not overdosed at the outside of the packages or under dosed at the centre. In a four-hour exposure period, rapid stirring for one hour at the beginning of the treatment was, to all intents and purposes, as effective as continuous stirring for the whole time.

Sorption

A very important factor affecting the action of fumigants is the phenomenon known as sorption. It is not possible in this manual to give a complete explanation of sorption, because the interaction of all forces involved is complex. Fortunately, for the purpose of understanding fumigation practice, it is possible to give a general account of the important factors concerned. In the relationship of gases to solids, sorption is the term used to describe the total uptake of gas resulting from the attraction and retention of the molecules by any solid material present in the system. Such action removes some of the molecules of the gas from the free space so that they are no longer able to diffuse freely throughout the system or to penetrate further into the interstices of the material. In fumigation practices, collision with air molecules tends to slow down gaseous diffusion through the material and sorption takes place gradually. Thus, there is a progressive rather than immediate lowering of the concentrations of the gas in the free space.

The curves for each of the four compounds clearly show the differences in degree of sorption of the fumigants by the same load in the chamber. Throughout the exposure period of six hours, the fall in concentration of methyl bromide was proportionately less compared with that for the three other fumigants, both in the empty chamber and with the two loads of oranges. This was due to the fact that the internal surface of the chambers and the boxes of oranges both sorbed less of the methyl bromide than of the other gases in proportion to the applied dosage. Sorption under a given set of conditions determines the dosage to be applied, because the amount of fumigant used must be sufficient both to satisfy the total sorption during treatment and also to leave enough free gas to kill the pest organisms. The general term sorption covers the phenomena of adsorption and absorption. These two are reversible because the forces involved, often referred to as van der Waal's forces, are weak. On the other hand, a stronger bonding called chemisorption usually results in chemical reaction between the gas and the material and is irreversible under ordinary circumstances.

Phvsical sorption

From the point of view of practical fumigation, adsorption and absorption, being both physical in nature and reversible, may be discussed in this manual under the heading of physical sorption. However, it is necessary to make some distinction between them at the outset because the forces involved may be less with adsorption than with absorption. Stated briefly, adsorption is said to occur when molecules of a gas remain attached to the surface of a material. Because some absorbents, such as charcoal or bone meal, are highly porous bodies with large internal surfaces, adsorption may also occur inside a given body.

Absorption occurs when the gas enters the solid or liquid phase and is held by capillary forces that govern the properties of solutions. For instance, a gas may be absorbed in the aqueous phase of grain or in the lipid phase of nuts, cheese or other fatty foods.

Physical sorption, considered generally, is an extremely important Factor affecting the successful outcome of fumigations. Apart from specific reactions between certain gases and commodities, it may be stated as a general rule that those fumigants with higher boiling points tend to be more highly sorbed than the more volatile compounds.

Physical sorption varies inversely as the temperature, and is thus greater at lower temperatures. This fact has important practical applications. It is one of the reasons why dosages have to be progressively increased as the temperature of fumigation is lowered.

Sorption may also be influenced by the moisture content of the commodity being fumigated. This was demonstrated by Lindgren and Vincent in the fumigation of a number of foodstuffs with methyl bromide; at higher moisture contents more fumigant was sorbed. This effect may be important with fumigants which are soluble in water to any significant degree.

The specific physical reaction between a given gas and a given commodity cannot be accurately predicted from known laws and generalisations. Usually, a certain fumigant must be tested with each material concerned before a recommendation for treatment can be drawn up.

Desorption

When a treatment is completed and the system is ventilated to remove the fumigant from the space and the material, the fumigant slowly diffuses from the material. This process is called Resorption and is the reverse of physical sorption. With the common fumigants and the commodities usually treated, residual vapours are completely dissipated within reasonable periods, although the length of time varies considerably according to the gas used and the material treated. Because of the inverse effect of temperature, dissipation of the fumigant usually takes place more slowly when the material is cold and may be hastened by warming the space and its contents.

Humidity also facilitates desorption of fumigants; at high humidity, wheat fumigated with ethylene dibromide was found to desorb 80 percent more of the fumigant than at very low humidity. As humidities can change appreciably with changing temperature, the rate of desorption may be dependent on the combined effect of both factors. Removal of desorbing gas can be speeded up by employing fans and blowers to force fresh air through the material. Natural ventilation may be hastened by taking the goods out of doors where advantage can be taken of wind, thermal air currents and the warming effect of sunlight. Some of the residual fumigant, usually small in quantity, may not be desorbed because of chemical reaction with the material.

Chemical reaction

If chemical reaction takes place between the gas and the material, new compounds are formed. This reaction is usually characterised by specificity and irreversibility. If the reaction is irreversible, permanent residues are formed. Examples are the reaction between hydrogen cyanide (HCN) and the reducing sugars in dried fruits with the formation of cyanohydrins or the appearance of inorganic bromide compounds after treatment of some foodstuffs with methyl bromide.

Because this type of reaction is essentially chemical it may be expected that its intensity varies directly with the temperature. This assumption has been confirmed by observation. Dumas has reported proportionately less fixed bromide residues in fruits as the temperature of fumigation was reduced from 25 to 4°C. Lindgren et al found an increase in the bromide content of wheat as the temperature during fumigation rose from 10 to 32°C.

Residue tolerances

In recent years attention has been focussed on the nature and possible effects on human beings of insecticidal residues appearing in foodstuffs. World-wide interest in this problem is reflected in the fact that international organisations such as the Food and

Agriculture Organisation of the United Nations (FAO) and the World Health Organisation (WHO) have set up special committees to investigate and report on the nature and significance of residues formed in foodstuffs as the result of the application of pesticides at different stages (as seed dressings, during growth, storage, transportation, etc.) prior to human consumption. These special committees review a number of pertinent factors involved in the use of each pesticide. Important factors, among others, are the toxicological significance of any residues formed and the average fraction of the total diet likely to be constituted by a food containing this residue. Through their Codex Alimentarius Committee these organisations undertake "to recommend international tolerances for pesticide residues in specific food products." Such recommendations are not binding on Member Nations of these organisations but are intended to be used as guides when particular countries are formulating their own regulations for pesticide residue tolerances.

Other Effects on Materials

Apart from the question of significant residues in foodstuffs, there is the problem of other effects which have a direct bearing either on the choice of the particular fumigant or on the decision as to whether fumigation is possible at all. The main types of reaction may be summarised as follows:

Physiological effects

1. Nursery Stock and Living Plants
    (a) Stimulation of growth
    (b) Retardation of growth
    (c) Temporary injury and subsequent recovery
    (d) Permanent injury, usually followed by death
2. Seeds
    (a) Stimulation of germination
    (b) Impairment or total loss of germination
    (c) Poor growth of seedlings from germinated seeds
3. Fruit and Venetables
    (a) Visible lesions
    (b) Internal injury

   (c) Shortening of storage life
   (d) Delay of ripening
   (e) Stimulation of storage disorders

4. Infesting Organisms
   (a) Death
   (b) Stimulation of growth or metamorphosis
   (c) Delay in development
   (d) Stimulation of symptoms of disease (so-called "diagnostic effect")

Physical and chemical effects on nonliving materials

1. Production of foul or unpleasant odours in furnishings or materials stored in premises.
2. Chemical effects that spoil certain products (for example, some fumigants render photographic films and papers unusable).
3. Reaction with lubricants followed by stoppage of machinery (clocks will often stop after fumigation with HCN).
4. Corrosive effects on metals (phosphine reacts with copper, particularly in humid conditions).

Dosages and concentrations

There should be a clear understanding of the difference between dosage and concentration. The dosage is the amount of fumigant applied and is usually expressed as weight of the chemical per volume of space treated. In grain treatments, liquid-type fumigants are often used and the dosage may be expressed as volume of liquid (litres or gallons) to a given volume (amount of grain given as litres or bushels) or sometimes to a given weight (quintals, metric tonnes or tons).

From the moment that a given dosage enters the structure being fumigated, molecules of gas are progressively lost from the free space either by the process of sorption and solution described above or by actual leakage from the system, if this occurs. The concentration is the actual amount of fumigant present in the air space in any selected part of the fumigation system at any given time. The concentration is usually determined by taking samples from required points and analysing them. It may thus be said that the dosage is always known because it is a pre-determined quantity. Concentration has to be determined because it varies in time and position according to the many modifying factors encountered in fumigation work. Three methods of expressing gas concentrations in air are in common use: weight per volume, parts by volume and percent by volume.

Weight per volume

For practical designation of dosages, this is the most convenient method because both factors—the weight of the fumigant and the volume of the space—can be easily determined. In countries using the metric system, this is usually expressed in grammes per cubic metre (g/m^3), whereas in countries using the British system of weights and measures, expression is usually in terms of pounds or ounces avoirdupois (avdp) per 1 000 cubic feet (lb/1 000 ft^3 or oz/1 000ft). By a fortunate coincidence in units of measurement, grammes per cubic metro are, for all practical purposes, equal to ounces per thousand cubic feet. Thus, recommended dosages can readily be converted from one system to the other.

Parts or percent by volume

Parts by volume and percent by volume will be discussed together because both modes of expression give the relative numbers of molecules of gas present in a given volume of air. The values for both modes have the same digits, but the decimal points are in different places (3 475 parts per million by volume of a gas is the same as 0.3475 percent by volume). Parts per million of gases in air are used in human and mammalian toxicology and in applied industrial hygiene. Percent by volume is used in expressing the flammability and explosive limits of gases in air.

Calculations for conversion of concentration values

By means of simple calculations giving useful approximations, values may be converted from weight per volume to parts by volume and vice versa. These calculations take into account the molecular weight of the gas and the fact that, with all gases, the gramme molecular weight of the substance occupies 22.414 litres at 0°C and 760 millimetres pressure.

A. To convert grammes per cubic metre (or milligrammes per litre or ounces per 1 000 cubic feet) into parts by volume.

1. Divide the given value by the molecular weight of the gas and multiply by 22.4; the resulting figure is the number of cubic centimetres (cm) of gas per litre of air.
2. One thousand times the figure obtained is the value in parts per million by volume.

3. One tenth of the figure obtained in (1) is the percentage by volume.

B. To convert parts per million (or percentage of volume) of gases to grammes per cubic metre (or milligrammes per litre or ounces per 1 000 cubic feet):

1. Divide the parts per million by 1 000, or multiply the percentage by ten to give the number of cubic centimetres of gas per litre of air.
2. Multiply this figure by the molecular weight of the gas in question and divide by 22.4. Comparative figures for weights and volumes at various levels have been calculated for the important gases, and these are given in the tables accompanying the subsequent discussion of each particular gas.

Concentration X time (c x t) Products

Most fumigation treatments are recommended on the basis of a dosage given as the weight of chemical required for a certain space—expressed as grammes per cubic metre or pounds per 1 000 cubic feet or as volume of liquid applied to a certain weight of material—expressed as litres per quintet or gallons per 1 000 bushels. Usually, this designation of dosage is followed by a statement of the length of the treatment in hours and the temperature or range of temperature at which the schedule will apply.

While such recommendations are usually based on treatments that have proved successful under certain conditions, they should also take into account the fact that certain factors may modify the concentrations left free to act against the insects. One important factor already mentioned is the effect of loads of different sizes. Another is the leakage from the structure undergoing treatment. What is really important is the amount of gas acting on the insects over a certain period of time. For instance, it is known (Bond and Monro, 1961) that in order to kill 99 percent of larvae of Tenebroides mauritanicus (L.) at 20°C, a concentration of 33.2 milligrammes per litre of methyl bromide must be maintained for 5 hours.

The product 33.2 milligrammes per litre x 5 hours = 166 milligrammes per litre x hours is known as the concentration x time product needed to obtain 99 percent control of this insect. It can be abbreviated and referred to as the c x t product. In the literature it is often expressed numerically with the notation mg h/l (milligramme hours per litre) In this example it would be known as the lethal dose for 99 percent of the population, or the LD.

In order to apply this method of treatment designation to practical fumigations, it is necessary to make reasonably correct determinations of the fumigant concentrations required to kill the insects under certain specific conditions; important modifying conditions are temperature and humidity.