

# Principles of (phosphine) fumigation



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# Insect management with chemicals

- **Protectants** (residual products for uninfested commodity)
  - Preventive
  - Residues persist for 1-2 years
  - May or may not control insects
  - Applied only once in the life time of a commodity
- **Fumigants**
  - Curative or responsive (for infested commodity)
  - Common option for commodities in the marketing system or supply chain where storage time is very short
  - Multiple applications can be made if needed
  - But damage becomes cumulative

Protectants are directly applied to the grain stream







- Calibration is essential
- Calibration
  - Grain flow rate
  - Volume of insecticide/ton of grain



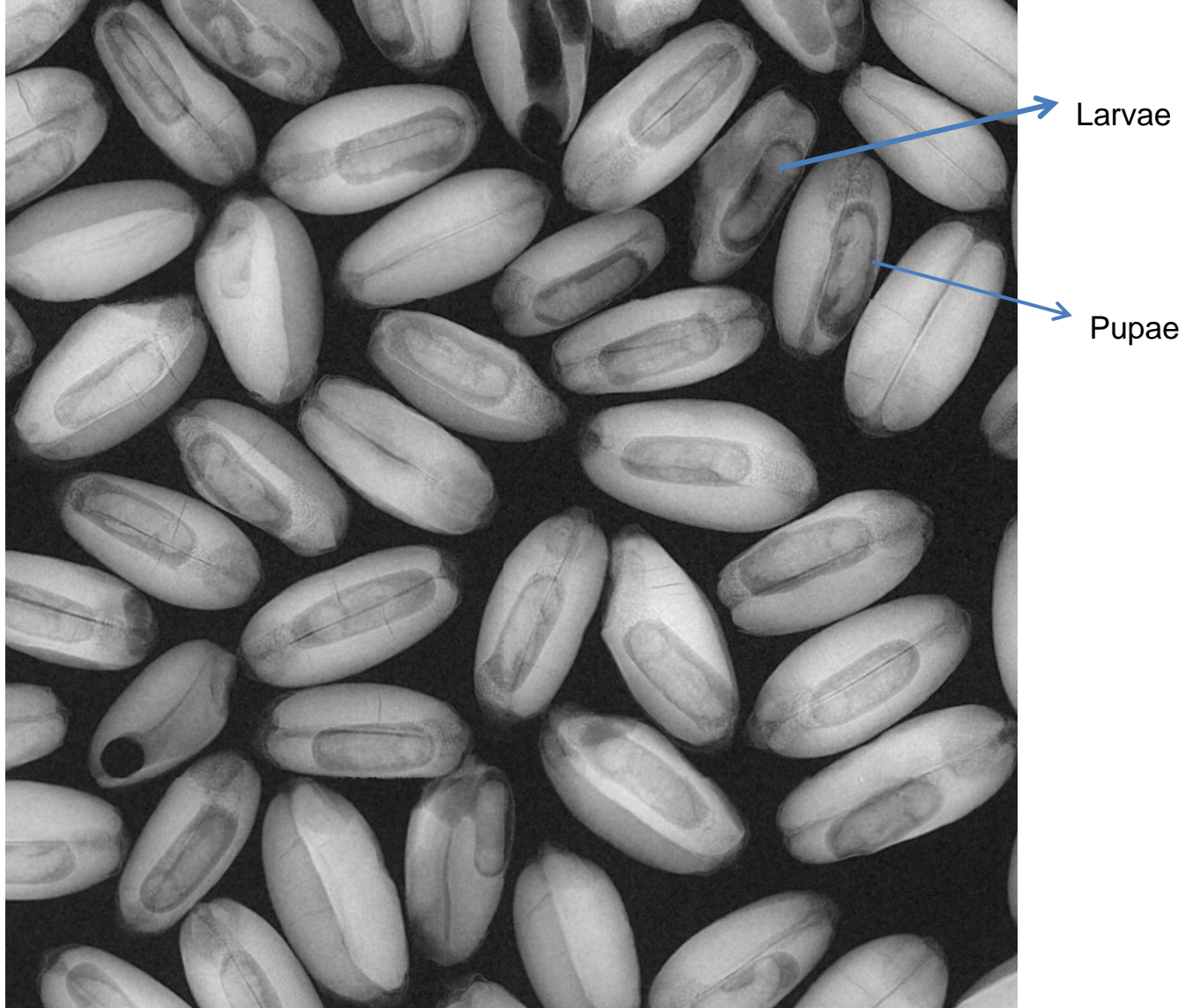






**Not recommended if grain is already infested**

**Protectants do not kill internal stages of insects**



Radiograph showing internal stages of insects within wheat kernels (Lesser grain borer)

# Issues with protectants: residues

- Protectant use results in insecticide residues that cannot be removed
- Co-mingling of untreated and treated lots results in lowering residues in commodity in the marketing channel
- How they are applied determines if Maximum Residue Limits (MRLs) are exceeded



# Applicator and food safety issues

- Directive 91/414/EEC in EU regarding pirimiphos methyl (Actellic) and other liquid protectants
  - Issues with applicator safety and residues
  - There is documented resistance in stored-grain insects to Actellic, especially the lesser grain borer
- Residues affect international trade
- ISO 22000
  - ISO 22000 specifies requirements for a food safety management system where an organization in the food chain needs to demonstrate its ability to control food safety hazards in order to ensure that food is safe at the time of human consumption

# Resistance in insects to protectants

- There is overwhelming evidence of insect resistance to grain protectants, including deltamethrin in Brazil
- Resistance to protectants is a worldwide problem
- Many countries have gone through several classes (groups) of pesticides because of resistance
  - organophosphates, pyrethroids, insect growth regulators (methoprene)
- Resistance to one pesticide confers resistance to other related products
- Once resistance develops, the product is no longer effective against insects

# Alternatives to protectants

- Sanitation (cleaning grain)
- Aeration (natural air)
- Chilling (chilled air)
- Fumigation (primarily with phosphine)



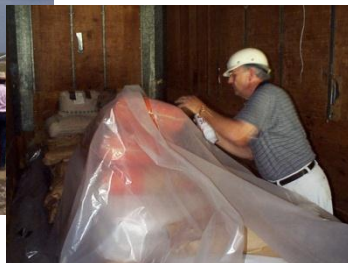
# Qualities of an effective fumigant

- Highly toxic to all life stages of insects
- Readily available and economical to use
- Imparts no harmful residue to commodities
- Nonflammable, noncorrosive, and nonexplosive under normal application conditions
- Noninjurious to product quality, seed germination, and end-use quality
- Highly volatile with excellent penetration properties and easy to aerate
- No adverse effect on the environment

# Phosphine is a viable alternative to protectants.....

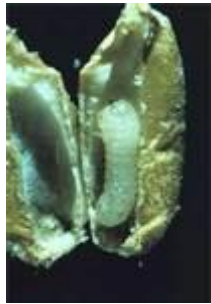
- If.....
  - Insects are resistant to protectants
  - If insecticide residues in commodities are undesirable
  - If your buyer wants assurances for an insect-free and insecticide residue-free commodity
  - If government regulations restrict admixing insecticides with commodities (e.g., India)
  - If repeated economical treatments are needed
  - **If grain is already infested!**

# Phosphine can be used to treat grain stored in various structures





Fumigation is only practical way to kill internal insects or insects deep within the grain mass



- Fumigants: work in the gaseous phase
- Have great penetration ability
- Dissipate quickly, leaving no meaningful residue
- Highly toxic by inhalation
  - Colorless, odorless gases
- Highly regulated
  - Federal and state laws governing use

# Hydrogen phosphide or phosphine (PH<sub>3</sub>)

- Metal phosphides
  - Aluminum phosphide
  - Magnesium phosphide
  - Inert ingredients
    - Ammonium carbamate
    - Ammonium bicarbonate
    - Urea
    - Paraffin wax
    - Calcium (impurity)
    - Sodium (impurity)
    - Heavy metals (impurity)

# All Aluminum Phosphide Formulations are not equal

- Purity and quality of raw materials
- Degassing and spent residue in flasks/sachets
- Quick release of gas during application (safety to applicators)
- Temperature attained during gas release (70°C, flash point)-ignition temperatures should never occur during application
- Hardness of the formulations (tablets and pellets)
- Sachets with appropriate fabric
- Use of red phosphorous, not yellow or white, to produce a greyish color product



# Properties of Phosphine

Formula	PH <sub>3</sub>
Molecular weight	34
Boiling point (°C)	-87.0
Specific gravity (gas) (air=1.0)	1.17
Vapor pressure (mmHg) at 30°C (1 atm)	42.0
Conversion factor (g/m <sup>3</sup> to ppm, 30°C and 1 atm)	730.0
Conversion factor (mg/L to ppm, 30°C and 1 atm)	719.0
Flammability limits in air (v/v)	1.79%
Solubility in water (v/v)	0.2

# Aluminum phosphide

## Different formulations for different uses

- Tablets
  - 3 g, releases 1 g of phosphine
- Pellets
  - 0.6 g, releases 0.2 g of phosphine
- Sachets
  - 34 g, releases 11 g of phosphine
- Linear gas generation until 80%, then the generation becomes nonlinear
- Gas release differences among formulations
  - Pellets > tablets > sachets



# Cytec's ([www.cytec.com](http://www.cytec.com)) phosphine fumigant gases

## **ECO<sub>2</sub>FUME<sup>®</sup>**

2% PH<sub>3</sub> (wt) in 98% CO<sub>2</sub>



## **VAPORPH<sub>3</sub>OS<sup>™</sup>**

100% PH<sub>3</sub> for on-site dilution



Cylinderized phosphine  
2% PH<sub>3</sub> and 98% CO<sub>2</sub>

# Advantages of cylinderized phosphine gas

- External application
- Eliminate confined space entry
- No waste by-products or residues
- No waste deactivation or disposal
- Ease of application and control
- Decreases amount of  $\text{PH}_3$  applied



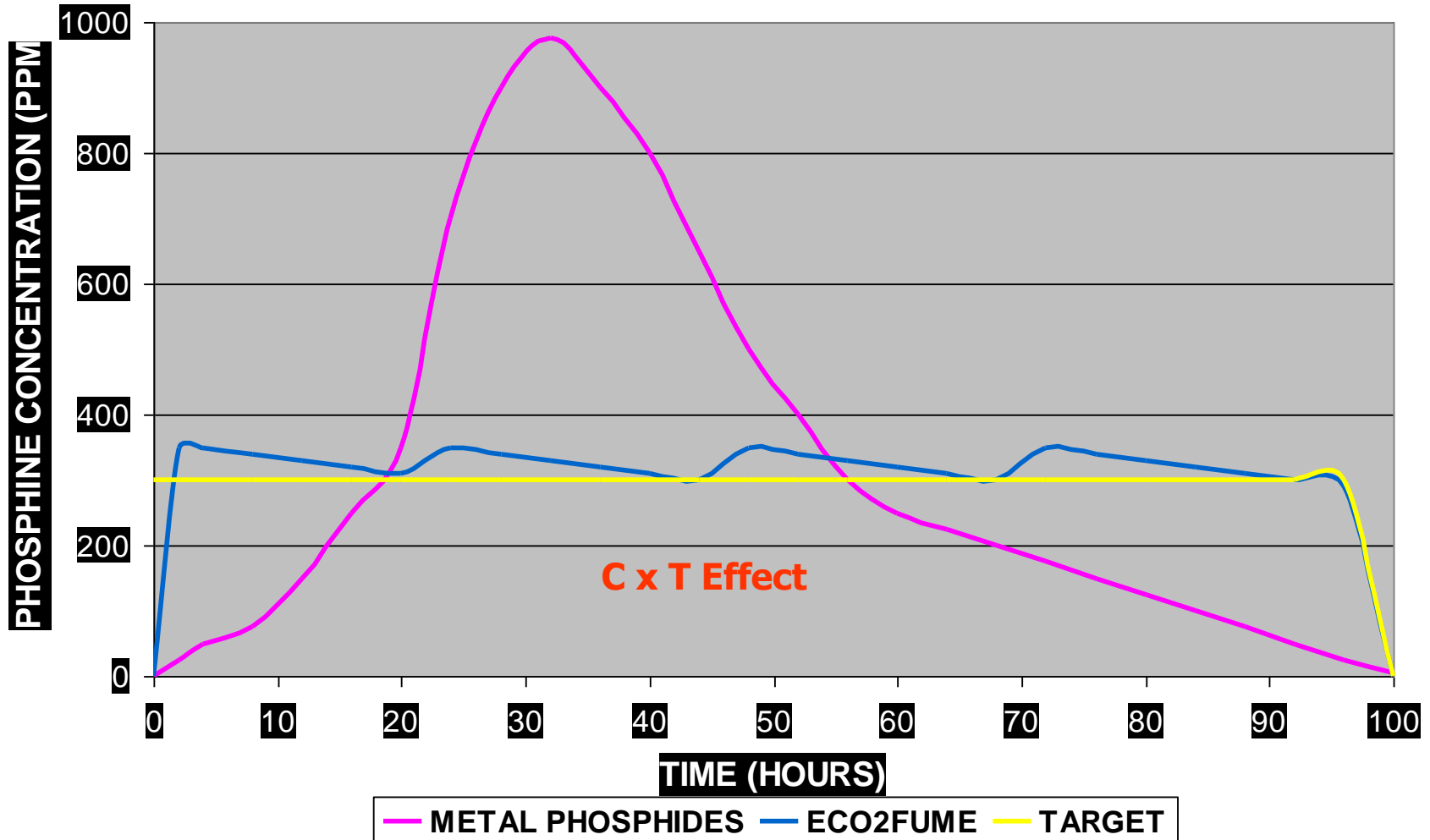
# Reduced worker exposure



Eliminates removal and deactivation of partially spent fumigants

# Reduce PH<sub>3</sub> usage and control

## CONCENTRATION VS TIME

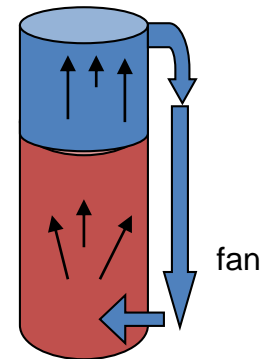


# Fumigation methods

- Direct application to commodities
- Automatic dispenser (at elevators)
- Probe using a PVC pipe
- Recirculation methods (for bins)



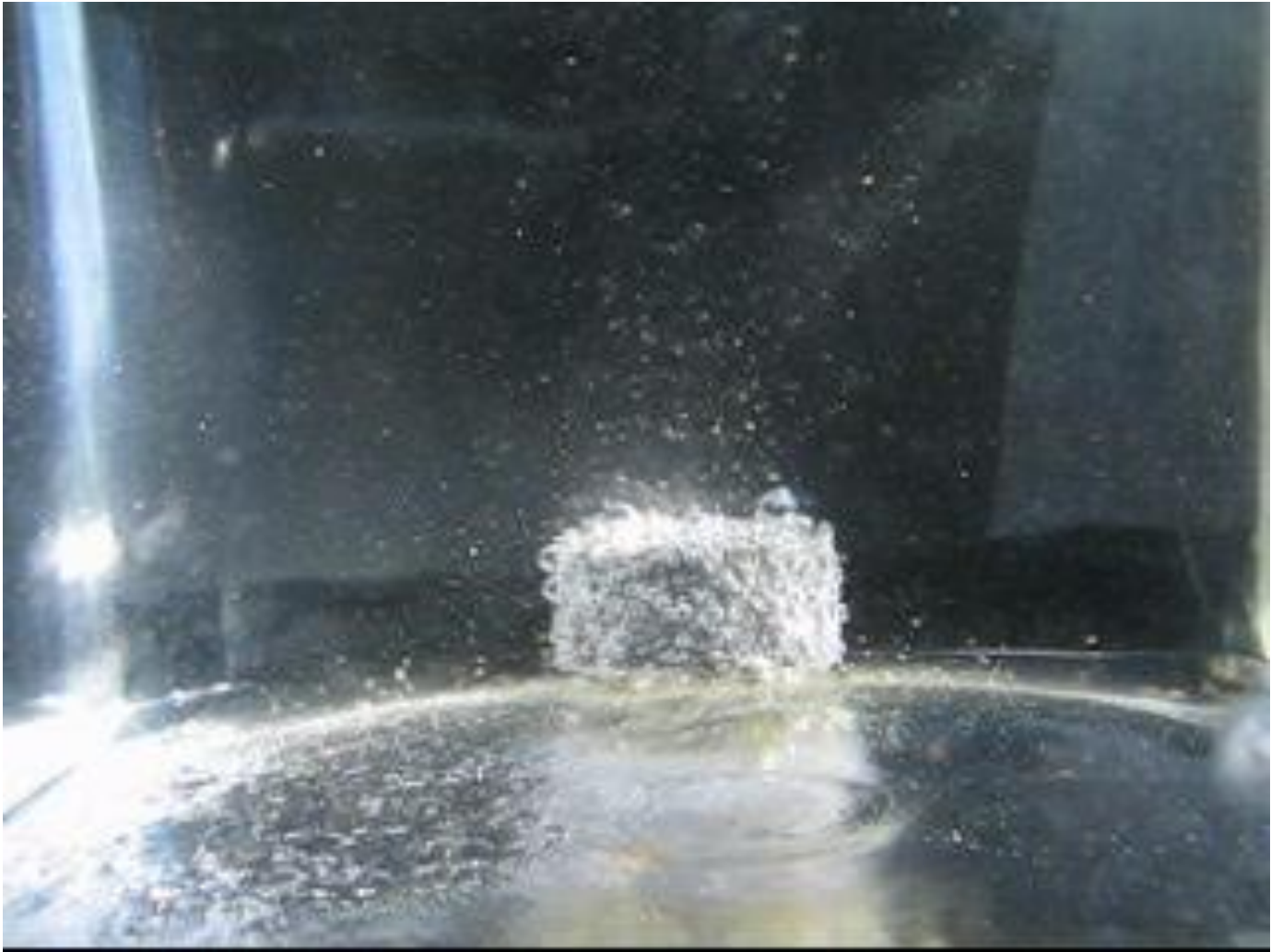
Recirculation Concept



# Gas release

- Upon exposure to air aluminum phosphide pellets, tablets and bags begin to react with atmospheric moisture
- Reaction starts slowly, gradually accelerates and then tapers off
- Reaction time for gas release will vary depending on the moisture and temperature





# Gas release is influenced by temperature and moisture

- At 50°F (10°C)

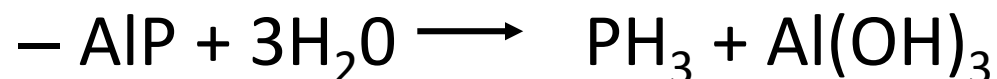
- PH<sub>3</sub> is produced 2.3 times faster in 15% moisture wheat than in 10% moisture wheat
- PH<sub>3</sub> is produced 1.5 times faster in 18% moisture corn than in 13% moisture corn

- At 86°F (30°C)

- PH<sub>3</sub> is produced 1.9 times faster in 15% moisture wheat than in 10% moisture wheat
- PH<sub>3</sub> is produced 1.3 times faster in 18% moisture corn than in 13% moisture corn

# Gas release

- Aluminum



- Mangesium (faster gas release than AlP)



Spent hydroxides have 0.5-1.0% of  $\text{PH}_3$  (another quality factor!)

# Factors affecting toxicity

- Concentration
  - (ppm, g/m<sup>3</sup>, or mg/L for a given level of kill at a given temperature, after a given exposure time)
  - Expressed as lethal dose (LD) to kill 50%, 90%, 95%, or 99% of the population
- Exposure time
- Life stage of insect exposed
- Insect species
- Grain temperature

Mode of action: Interferes with respiration; interrupts processes that provide energy to living cells



# Stage-specific susceptibility to phosphine, Granary weevil, *Sitophilus granarius*

<b>Stage</b>	<b>LD<sub>50</sub> (ppm)</b>	<b>LD<sub>99</sub> (ppm)</b>
Egg	18	109
Young larva	Not tested	Not tested
Old larva	3	16
Pupa	22	1,088
Adult	4	9

Tests conducted at 80°F (27°C) for 2 days

# Temperature affects lethal dose of phosphine

<b>Temperature</b>	<b>LD<sub>90</sub></b>	<b>LD<sub>99</sub></b>
59°F, 15°C	0.07 mg/L, 48 ppm	Not tested
77°F, 25°C	0.26 mg/L, 187 ppm	0.79 mg/L, 567 ppm
86°F, 30°C	0.05 mg/L, 38 ppm	0.37 mg/L, 280 ppm

Concentrations required to kill the most-resistant stage (pupa) of the granary weevil in 2 days

# Temperature vs fumigation time

Temperature	Pellets	Tablets	Bags
Below 4.4°C	DO NOT FUMIGATE		
5.0 – 11.7°C	8 days	10 days	14 days
12.2 – 15.0°C	4 days	5 days	9 days
15.6 – 20.0°C	3 days	4 days	6 days
20.6 – 25.0°C	2 days	3 days	4 days
Above 25°C	2 days	3 days	3 days



# Lethal dose of phosphine varies with the insect species

77°F (25°C), 4-day exposure

<b>Species</b>	<b>Most-tolerant stage</b>	<b>LD<sub>90</sub></b>	<b>LD<sub>99</sub></b>
Rice weevil ( <i>Sitophilus oryzae</i> )	Pupa	0.044 mg/L, 32 ppm	0.086 mg/L, 62 ppm
Lesser grain borer ( <i>Rhyzopertha dominica</i> )	Egg	0.026 mg/L, 19 ppm	0.085 mg/L, 62 ppm
Flat grain beetle ( <i>Cryptolestes pusillus</i> )	Egg	0.026 mg/L, 19 ppm	0.046 mg/L, 33 ppm

# Increasing the exposure time decreases the lethal dose of phosphine for a given mortality

Species	Mortality	2 Days	4 Days	7 Days
Rice weevil ( <i>S. oryzae</i> )-Pupa	90%	0.083 mg/L, 60 ppm	0.044 mg/L, 32 ppm	0.022 mg/L, 16 ppm
Maize weevil ( <i>S. zeamais</i> )-Pupa	90%	0.40 mg/L, 287 ppm	0.04 mg/L, 29 ppm	0.013 mg/L, 9 ppm
Lesser grain borer ( <i>R. dominica</i> )-Egg	99%	0.79 mg/L, 567 ppm	0.097 mg/L, 70 ppm	0.013 mg/L, 9 ppm



# Dosage recommendations

- Label doses result in concentrations that exceed information shown in previous tables
- Based on volume ( $1.5 \text{ g/m}^3$ )
  - 3 tablets/ton of grain
- Concrete silos
  - 770 to 3,590 ppm
- Metal bins
  - 1,750 to 3,625 ppm

The prescribed doses compensate for losses due to leakage, non-uniform diffusion, and sorption!

# Effective Phosphine Fumigation is a Challenge in Outdoor Stacks



Wind forces cause  $\geq 30\%$  gas loss rate in outdoor stacks



# Sealing is key for safe and effective fumigation

- Glue
- Plastic (4 mil; 1 mil = 0.25 micrometer)
- Tape
- These materials are cheap!!!



where gas loss occurs





# Effective floor sealing is vital in stack treatments with phosphine



# Phosphine gas outside covered stacks during fumigation ANGRAU-KSU Collaborative Study, India

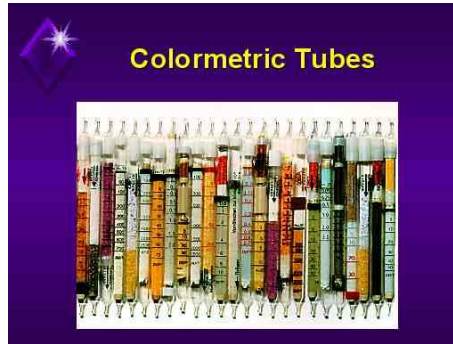
Place	Date of monitoring	Godown	stack particulars	Date of fumigation	Date of uncovering the stack	Concentration of Phosphine in ppm
Karlapalem	22-2-10	APSWC	5A-8			255
Karlapalem	22-2-10	APSWC	5B-7			260
Ongole	25-2-10	FCI	3B6-80	22-12-09	29-12-09	387
Ongole	25-2-10	FCI	3B1-83	25-01-10	30-01-10	376
Ongole	25-2-10	FCI	2B10-86	28-01-10	03-02-10	368
Ongole	25-2-10	FCI	1A3-98	05-02-10	10-02-10	361
Ongole	25-2-10	FCI	1A8-108	03-02-10	10-02-10	357
Bapatla	06-3-10	APSWC	1A-1			288
Bapatla	06-3-10	APSWC	1A-4			254
Bapatla	06-3-10	APSWC	1A-6			280
Bapatla	06-3-10	APSWC	1A-7			251
Ongole	10-3-10	FCI	1A-1	05-3-10	12-3-10	1085
Ongole	10-3-10	FCI	1A-7	05-3-10	12-3-10	1685
Ongole	10-3-10	FCI	2B-2	04-3-10	11-3-10	545
Ongole	10-3-10	FCI	2B-6	05-3-10	12-3-10	189
Ongole	10-3-10	FCI	3C-6	05-3-10	12-3-10	981



# Gas monitoring is essential

- During application
- During fumigation
- After fumigation

- Effectiveness against insects
- For applicator/worker safety



- *Miniwarn* – Four Gas Unit
- *Pac III* – Single gas unit
- *Pumps* – Detects Gas levels
- *Colormetric Tubes* – Draeger, Matheson, MSA



# Fumigation monitoring



# Who needs to use monitoring equipment?

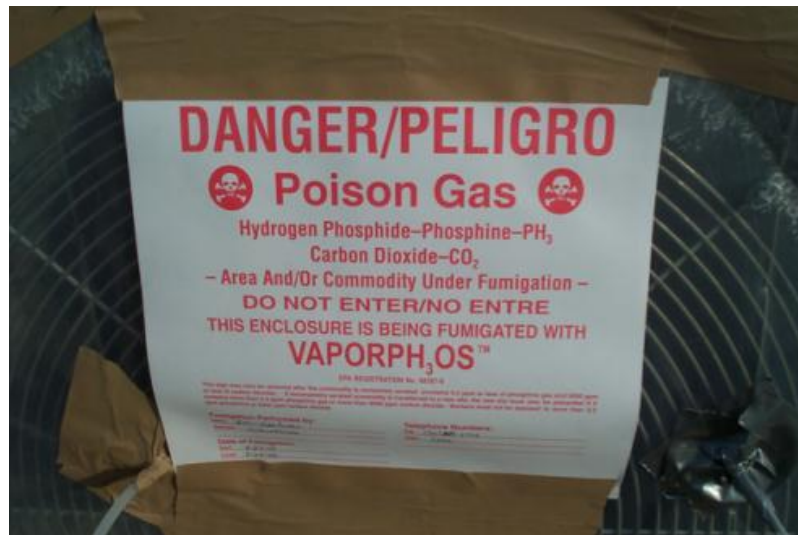
- Anyone entering a fumigated site
- Employees applying fumigant
- Anyone who may enter a possible fumigation site
- Anyone who is responsible for daily gas readings during fumigation





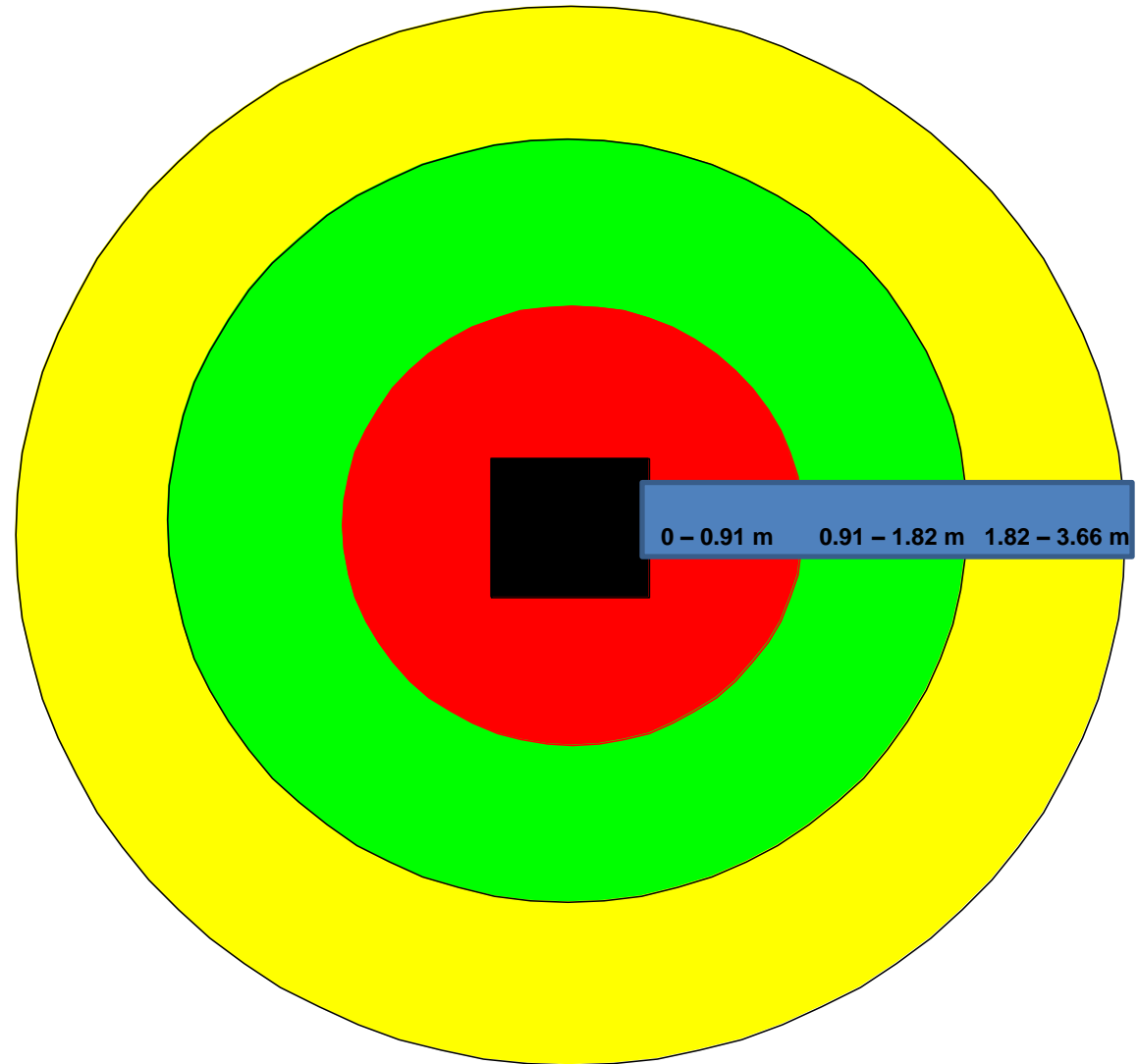
# Placard fumigated site

- Placard fumigated site entrances
- Site security, locked entrances, sometimes extra guards



# Where to monitor for gas outside

If zero reading at 0-0.91 m no reading required at any other distances



Test Around all:

- Vents
- Fans
- Tunnels
- Doors
- Any other suspected areas

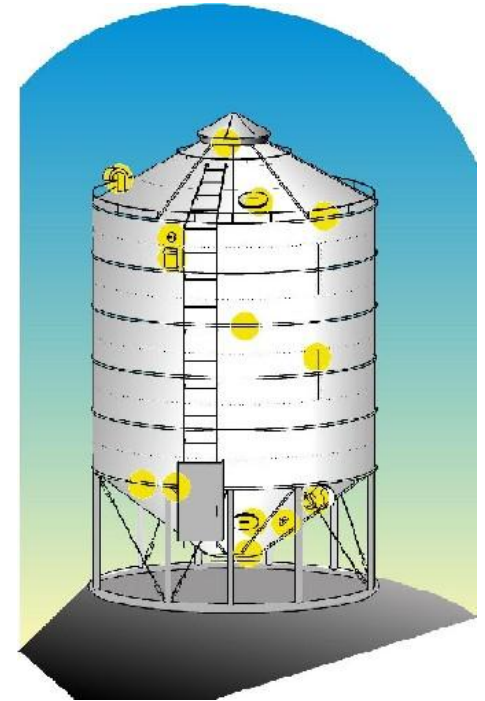
# Maintenance of monitoring equipment

- All maintenance shall be done as according to all manufacturer specifications
- SafetyQuip – can service and calibrate monitoring equipment



# Keys to successful fumigation

- Minimize gas losses by making fumigated area relatively gas tight
- Monitor gas concentrations during fumigation (in ppm)
- Follow all safety precautions
- Plan and fumigate for longer rather than shorter durations
  - Good quality fumigant
  - Understand temperature and moisture interactions
  - Evaluate and revise application techniques



# Insect resistance to phosphine

- Insects acquire resistance if exposed to sublethal concentrations
  - Short-duration fumigations (3 days or less)
  - Leaky structures
- Field failures may or may not be due to resistance
- Realistic assessment of resistance needs to be confirmed under field conditions
- Insects resistant to phosphine CAN BE controlled with phosphine by increasing the exposure time!!!

# Storage Guidelines and Signage



- Basic requirements for any pesticide storage include signage, security, ventilation, good housekeeping, and others.
- Codes will vary depending on materials in the storage. Severe (4) Health and flammability hazards; moderate (2) reactivity. *Do not use water to put out phosphine fires*





# Respiratory protection is essential

Employer must select and provide an appropriate respirator based on the respiratory hazards to which the worker is exposed and workplace and user factors that affect respirator performance and reliability



# Phosphine: distinctive odor and concentration levels for safety

- Phosphine has a garlic-like odor!  
***Odor is not a reliable means of detection*** but may be a helpful warning
- 0.3 ppm is time-weighted average threshold limit value for 8 h workday.
- 1.0 ppm is short term exposure limit for 15 minutes
- 0.3 – 15 ppm is range where respirators are used
- 15 ppm+ or unknown concentrations require SCBA
- 50 ppm immediately dangerous to life and health
- Fumigation levels usually at 200 ppm or higher



# Respirators

- Different fumigants and concentrations call for different protective equipment: maybe nothing; full face respirator with appropriate cartridge; or a self contained breathing apparatus (SCBA)
- For most grain fumigation operations with phosphine the respirator with an appropriate cartridge is adequate.
- ***Dust masks have no protective value against fumigants!***



# Fit testing

Before an employee uses any respirator with a negative or positive pressure tight-fitting face piece, the employee must be fit tested with the same make, model, style, and size of respirator that will be used.



# Qualitative fit test (QLFT)

A pass/fail fit test to assess the adequacy of respirator fit that relies on the individual's response to the test agent





# Quantitative fit Test (QNFT)

An assessment of the adequacy of respirator fit by numerically measuring the amount of leakage into the respirator





# Things to consider when using phosphine

- Do not allow aluminum phosphide to pile up
- Can result in ignition
- Spent residue should be buried in the ground
- Use all of the tablets/pellets in a flask
- Wear gloves to handle product



# Training and information

Employers must provide effective training to employees who are required to use respirators



# First aid

- Symptoms of exposure to phosphine are headache, dizziness, nausea, difficulty breathing, vomiting, and diarrhea. In case of overexposure get medical attention immediately

# If inhaled



- Move person to fresh air.
- If person is not breathing, call an ambulance, then give artificial respiration immediately, preferably by mouth-to-mouth if possible.
- Keep warm and make sure person can breathe freely.
- Call a poison control center or doctor for further treatment advice

# If on skin or clothing

- Brush or shake material off clothes and shoes in a well-ventilated area
- Allow clothes to aerate in a ventilated area prior to laundering
- Do not leave contaminated clothing in occupied and/or confined areas such as automobiles, vans, motel rooms, etc
- Wash contaminated skin thoroughly with soap and water



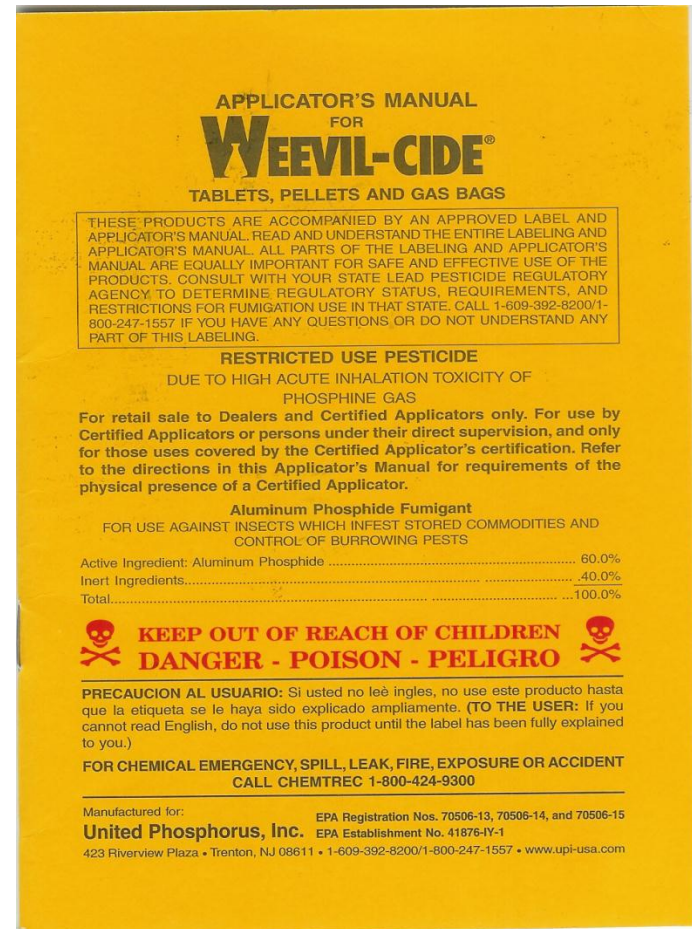
# If in eyes



- Hold eye open and rinse slowly and gently with water for 15 – 20 minutes
- Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye
- Call poison control center or doctor for further treatment advice

# Have a copy of the applicator's manual with you at all times

- If you have to take someone for medical attention. Make sure you take a current copy of the brand of aluminum phosphide you are using with you for the doctor or medical attendant



# “Desorption” or “off-gassing” is a potential concern for non-fumigators



- Fumigants penetrate commodities, and then it may take some time to dissipate
- Sometimes an atmosphere around a commodity that has recently been fumigated may seem to be aerated but concentrations will build up again when ventilation is stopped
- *Fumigators need to be aware and maintain monitoring for safety!*
- In grain elevators the gallery level, tunnels, and head houses could be susceptible

# Conclusions

- Phosphine has been the choice fumigant for more than 50 years
- It is an economic fumigant of choice for treating commodities
- Flexibility in application to various commodities
- Meets worldwide requirements for delivering commodities free of insecticide residues
- Follow good product stewardship and pest management programs to keep phosphine for the future
- Phosphine complements other pest management tactics

Thank you