Fungicides and Fertilizers Used for Disease Control: Chemistry and Use

MAAGCS Educational Seminar
20 March 2008
Fungicides

- Important disease management tools for all cultivated crops
- In almost all cases, fungicides are fungistatic
  - Active ingredient suppress, inhibit, or limit fungal development and growth
  - Does not ‘kill’ fungi
Types of Control

1. Preventive
2. Curative

- **Preventive**
  - Insurance policy—may not even get disease

Prevents infection (successful penetration and establishment in the host)
Must be in place before process begin
Types of Control cont.

- **Curative**
  - Some refer to as eradicative or rescue
  - Fungicide has activity after infection has already occurred
  - Curative-fungicide stops or suppresses
  - Eradicative-fungicide limits activity after the appearance

  - What to know!

  Preventive applications take place before outbreak or visible symptoms occur

  Curative applications take place after outbreak occurs

  Sometimes rates on label are dictated by type of control!

Turfgrass Disease Solutions, LLC
Fungicide Info

- Every fungicide has three names
  - Trade Name (most commonly used)
  - Chemical Name
  - Generic Name
Examples of 3 Name System

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Chemical Name</th>
<th>Generic Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daconil Ultrex 82.5WDG</td>
<td>tetrachloroisophthalonitrile</td>
<td>Chlorothalonil</td>
</tr>
<tr>
<td>Banner MAXX 1.3 MEC</td>
<td>1-((2-(2,4-Dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl)methyl)-1H-1,2,4-triazole</td>
<td>Propiconazole</td>
</tr>
<tr>
<td>Cleary’s 3336 4F</td>
<td>Dimethyl 4, 4-openylenebis-(3-thioallophanate)</td>
<td>Thiophanate methyl</td>
</tr>
</tbody>
</table>
Classification of Fungicides

Three Systems to Classify

1. Chemical Class (Structure)
2. Chemical Mode of Action
   - i.e. benzimidazoles
   - Restrict fungal DNA synthesis
   - etc,…
3. Activity on or in the plant
   (contact, penetrant, and systemic)
Target 1: **Microtubules** - Benzimidazoles (Benomyl and Thiophanate Methyl)
- Work by affecting spindle formation

Target 2: mitochondria
Strobilurons/flutolanil/boscalid/cyazofamid
Inhibit electron transport in specific stages

Target 3: Cell Wall- Polyoxin

Target 4: Cell Membrane
DMI/Dicarboximides/propamocarb
/PCNB/fludioxanil

Target 5: General Cell Constituents
Chlorothalonil

Target 6: Nucleic acid
mefenoxam

Fungicide applied

6 Cellular Targets

Slide adopted from R. Latin and Kaminski and Fidanza
Systemics: Phosphites and Fungicides

- Systemic- only one group of fungicides
- Systemic connotes translocation through entire plant
- Move in Xylem and Phloem
- Good Efficacy with Preventive Control
- Term Phophonates (carbon to phosphorus bond (C-P))
  - Includes: Phophonate Fungicides and Phosphite ‘Fertilizer’ or Supplemental Products
Systemics: Phosphonate Products

- Phosphonates: Some are made up of salts and esters of phosphorous acid $\text{HPO(OH)}_2$
- Phosphorous acid + water = phosphonic acid
- Phosphonic acid if applied to a plant would be extremely phytotoxic-tip burn and death
- Hence, reduced with an alkai salt such as KOH to produce POTASSIUM PHOSPHITE
**Systemics: POTASSIUM PHOSPHITE**

- Main ingredient in phophanate fungicides such as:
  - Magellan
  - Alude

These products have EPA labels, hence, cost more and labels must be followed-labeled for specific diseases.
POTASSIUM PHOSPHITE

- Is the main ingredient in most phosphanate fertilizer products
  - (some call phosphite fertilizers)
- **Many** on the market (Some Examples)
  - K-Phite (0-29-26)
  - Plant Food Phosphite 29 (0-29-26)
  - Ele-Max Foliar Phosphite (0-28-26)
  - Nutri-Phite P+K (0-28-26)
  - PK Plus (3-7-18) 14% phosphite
  - Starphite (Two different analysis-2-40-16; 0-28-26)
Green Flo™ Phyte

0-0-18

A Supplemental Fertilizer Solution for Stress Relief and Recovery

GUARANTEED ANALYSIS

Soluble Potash (K$_2$O) .................... 18%

DERIVED FROM: potassium phosphite.

KEEP OUT OF REACH OF CHILDREN

CAUTION - AVISO

READ LABEL CAREFULLY

PRECAUTIONARY STATEMENTS

Avoid prolonged or repeated contact with eyes, skin and clothing. Safety goggles or a full face shield should be worn. Wear appropriate protective equipment to protect skin, such as rubber or plastic aprons, rubber gloves and boots. Avoid breathing mist or vapor. Keep containers closed. Wash thoroughly after handling. May cause gastro-intestinal distress if swallowed.

FIRST AID

In case of contact with eyes, immediately flush eyes with water for at least 15 minutes. Seek immediate medical attention if irritation occurs. In case of skin contact, flush skin with water. If irritation occurs, seek immediate medical attention. Remove and wash contaminated clothing before reuse. If swallowed, give large amounts of water and induce vomiting by
Starphite

Potassium Phosphite Fertilizer

Guaranteed Analysis

Soluble Potash (K₂O): 26.00%

Derived from Potassium Phosphite

Caution

Not a source of Available Phosphorus.

*Not a source of Available Phosphorus.
Phosphonate ‘Fertilizer’ Products

- Do not have a fungicide label
  - Your risk

- Do have fungicidal properties
  - Under most circumstances= good control

- Some will list the % P on the label
  - Example
    - 2-0-16 in northeast region
    - 2-40-16 in mid-Atlantic region

  Most will state derived from potassium phosphite (
Phosphite versus *P. aphanidermatum*
Phosphate versus *P. aphanidermatum*
Other Phosphonate Fungicides

- Instead of treating the phosphonic acid with a salt, it could be treated with an ethanol to form ethyl phosphonate.
- Then treated with Aluminum ions to neutralize.
- This forms Fosetyl-Aluminum.
  - This is the active ingredient in Chipco (Alliette) Signature.
Summary: Two Phosphononates

1. Phosphonic acid
   + KOH = POTASSIUM PHOSPHITE
     (often referred to as mono and di potassium salts of phosphorous acid or phosphoric acid)

2. Phosphonic acid
   + ethanol = ethyl phosphonate
   + Aluminum ions= Fosetyl-Aluminum
     (Chipco Signature also has ‘stress guard pigment’)

$\text{H}_2\text{PO}_4^-$ = used by plants for energy (ATP, DNA, many functions)
$\text{H}_2\text{PO}_3^- = $ not the same = direct fungistatic effects on pathogens

The difference in one oxygen molecule makes a huge difference!
Phosphonate Compound – Salts and esters of phosphorus acid

Phosphorus Acid [(HPO(OH)₂)]

Water

Phosphonic Acid

Neutralize with alkali salt (ie. KOH)

Mono- and di- potassium phosphite (ie. KH₂PO₃)

Ethanol

Ethyl-Phosphonate

Neutralizing Al ions

Fosetyl-Al
Aluminum tris (O-ethyl phosphate) i.e. Signature Fungicide (With Green)

Slide courtesy of G. Kauffman
Possible confusion

- Should not be confused with phosphate-derived fertilizers such as:
  - Ammonium phosphate
  - Triple super phosphate

- Chemically these phosphates are similar, however, differ in how they act on fungi and plants.
- These actually have a P fertilizer credit-used for ATP.
## Classification of Phosphate Products

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cost</th>
<th>Pythium Control</th>
<th>Anthracnose Control</th>
<th>Turf Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium phosphate fertilizer</td>
<td>$</td>
<td>None</td>
<td>None</td>
<td>Highest</td>
</tr>
<tr>
<td>Potassium phosphite supplemental ‘fertilizer’</td>
<td>$</td>
<td>Good</td>
<td>Marginal- to Good- Prev</td>
<td>Yes</td>
</tr>
<tr>
<td>Potassium phosphite fungicide (Alude, Magellan, Vital, etc)</td>
<td>$$</td>
<td>Good (Labeled)</td>
<td>Marginal- to Good- Prev</td>
<td>Yes</td>
</tr>
<tr>
<td>Fosetyl-Al Signature</td>
<td>$$$</td>
<td>Good++ (Labeled)</td>
<td>Ok-Marginal</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Contact or Protectant Fungicides

- Only effective at site of contact or if deposit remains intact in high enough concentration
- Good coverage is essential (SV and Nozzle)
- Can be effective against germinating spores or active mycelium on surfaces they contact
- Do not penetrate plant or host tissues
  - Will not affect mycelium or fungal structures already established inside plant

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Contact Fungicides cont.

- Low solubility and should not be drenched into soils—rarely effective against root and crown diseases.
- Oftentimes broad spectrum in their control because of multi-site activity.
- Very low risk for resistance development
- Subjected to: weathering, mowing
- Relatively short application interval needed
Contact Fungicides

Dithiocarbamates

- **Broad Spectrum and Contact Activity;** Interferes With in Amino Acids
- **Thiram Fungicides;** Spotrete® and Thiram®
- **Mancozeb Fungicides;** Fore®, Dithane M-45®, and Manzate®, Protect
- **Maneb Fungicides;** Dithane M-22®
Dithiocarbamates

- Generally, provide good control of Dollar spot, Brown Patch and Foliar Diseases
- Short re-application interval needed
- ‘Fore Example’

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Contact Fungicides Cont.

- Phenopyrrole Chemistry

- An Antifungal Compound Derived From a Bacterium *Pseudomonas pyrocinia*

- Interferes With Fungal Membrane Transport

- Fludioxonil : Medallion
Fludioxonil: Medallion

- Broad Spectrum Control
  - Does not have activity on dollar spot
  - Good to Excellent: brown patch, anthracnose, dead spot, snow molds, gray leaf spot material
  - May improve performance of other fungicides
  - Low use rates 0.15-0.5 oz/1000ft²
Contact Fungicides

- **Benzonitriles or Nitriles**
- **Chlorothalonil ; Daconil®, Echo®, and Manicure®**
- **Broad Spectrum and Contact Activity; Affects many general fungal cell constituents**
- **Eye Irritation- big EPA issue**
Chlorothalonil

- Number one used fungicide in turf
- Rates and Application intervals restricted by the EPA
- Wide range of effective diseases
  - Excellent brown patch, anthracnose, dollar spot, dead spot, snow molds, gray leaf spot material
Contact Fungicide Continued

Aromatic Hydrocarbons

- Three Products in Turf
  - Chloroneb (Terramec)
  - Ethazol (Koban), or Etridiazole (Terrazole)
  - Quintozene (PCNB)

- Interferes With DNA Synthesis and Enzyme and Membrane (chitin) Production Needed for Growth and Reproduction
Chloroneb (Terramec)

- Contact fungicide used for control of *Pythium* blight and some snow molds
- Examples include:
  - Fungicide V 6G (3 to 5.9 lb/1000ft²),
  - Teremec SP 65W (4.0 oz/1000ft²)
  - others….
Ethazol (Koban) or Etridiazole (Terrazole)

- Used for Pythium control
- Best used for curative control (good knockdown), than apply a systemic or penetrant that will last longer
- Provides only short duration of control
Quintozone (PCNB)

- Effective against gray snow mold, pink snow mold, melting out diseases, brown patch, and dollar spot
- Frequently used in areas where long snow cover is typical
- Can cause some discoloration (phyto) when used in warmer areas (above 65°F)
- Relatively cheaper when compared to other snow mold materials…
Localized Penetrant

- Have some characteristics similar to contact fungicides (can affect germinating spores and suppress active mycelia on plant surfaces)
- Must contact surfaces
- Limited capacity to be absorbed into underlying tissues in concentrations effective for disease control
Localized Penetrant

- Translaminar in movement- move very short distances from the site of application, such as across a leaf blade from one surface to the other (Diffusion)
- More soluble than contact fungicides, however, few are effective against root pathogens
- Relatively Broad Spectrum
Localized Penetrant

- Considered ‘Site-specific’
- Many ‘at risk’ for resistance development
Localized Penetrant Fungicides

Dicarboximides

- Became Available in 1974-75
- Mode of Action: Activity at the Cell Membrane - Interferes with Cell Division and DNA And RNA Synthesis
Localized Penetrant

● Examples:
  - Iprodione: Chipco 26019®, 18 Plus, 26GT®, Iprodione Pro among others
  - Vinclozolin: Curalan®, and Touche®
Localized Penetrants

- Polyoxins Class
  - Endorse (Polyoxin-D)
    - Good to Excellent Fairy Ring, Brown Patch, Anthracnose material
    - No known resistance, yet!
Localized Penetrant

Strobilurins

- Currently, four strobiluron fungicides in turf and ornamental market
- Two are localized penetrants and two are acropetal penetrants
- Strobilurins (QoI) interfere with respiration by disrupting electron transport at the Quinol-oxidizing site of cytochrom bc in the mitochondria-resulting in impaired ATP

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Strobilurins

- Considered to be low-risk pesticides due to the fact that humans don’t have that pathway and that they are derived from a natural fungi

- This Class of Fungicides Mimic an Anti-Fungal Compound Found in Wood Decaying Fungi; Allelopathic Effect

- Single site activity
Localized Penetrant Strobilurins

- Compass®: trifloxystrobin
- Introduced in 1999
- A mesostemic broad spectrum
- Optimum control occurs in a preventative program
- Application rates vary from .1 to .25 oz/M
- Brown patch, summer patch, red thread, gray leaf spot
Localized Penetrant Strobilurins

- Insignia®: pyraclostrobin
- 2002 season
- A broad spectrum
- Optimum control occurs in a preventative program
- Application rates vary from .5 to .9 oz/M
- Brown patch, summer patch, red thread, gray leaf spot, Pythium, Dollar spot suppression, leaf spots-melting out
Unique Activity of Localized Penetrant Strobilurins

- Some also refer to these two localized penetrant strobilurins activity as mesostemic

- Trifloxystrobin- moves through vapor through leaves- can be redistributed (as Al metabolized other particles move into the leaf.

- Pyraclostrobin- translaminar movement moving across leaf tissue through diffusion-higher concentrations to lower. No vapor like Trifloxystrobin

Neither move significantly in the xylem!
Localized Penetrant

Cyazofamid

- **Segway**
  - Cyazofamid
  - Released in late 2006-early 2007
  - Labeled for Pythium (foliar and root dysfunction) and damping off
  - QIL-Quinone inside binding site acts closely to QoI fungicides—too date no cross resistance with QoI fungicides (such as Heritage, Insignia, Disarm, and Compass) has been documented.
Acropetal Fungicides

- Most effective against pathogens in plant
- Formulated to penetrant plant tissues rapidly so have little activity on surface
- Almost all of them move upward from the point of absorption

Acropetal movement= translocated only in the xylem
Acropetal Fungicides

- Once inside the plant, restrict fungal growth, and limit colonization by the pathogen and/or reduce its ability to reproduce.

- Move upward in vascular tissues-not downward

- Fairly soluble and most are effective against root, crown, foliar and rhizome diseases

- Site specific and ‘at risk’ for resistance
Acropetal Penetrants

Benzimidazoles

- First Acropetal Penetrant Fungicide
- Effective at Relatively Low Rates
- Inhibits Cell Division; Affects Microtubule (Spindel) Formation
- Tersan 1991: benomyl
- Fungo, Cleary 3336, TM, others: Methyl Thiophanate

Turfgrass Disease Solutions, LLC
Acropetal Penetrant Benzimidazoles T-Methyl and benomyl

- Generally, used to control:
  - Pink snow mold
  - Dollar spot
  - Brown patch
  - Gray leaf spot
  - Red thread
  - Summer patch
  - Anthracnose
Sterol Inhibitors or DMI’s

- Consist of Five Different Chemical Families, Two Have Labeling in Turf and Ornamentals
- Interfere With Ergosterol Synthesis
- Largest group of fungicides \((n=\text{currently 7, maybe more shortly})!\)
- Began to Come Into the Market During 1980’s
- Growth Regulating Effects

Turfgrass Disease Solutions, LLC
Sterol Inhibitors

- **Triazole Class:**
  - Banner® - Propiconazole
  - Bayleton® - Triadimefon
  - Sentinel® - Cyproconazole - off of the turf market
  - Eagle® - Myclobutanil
  - Lynx® - Tebuconazole*?
  - Tourney® - Metaconazole
  - Trinity® - Triticonazole
  - Trition® - Triticonazole*

  *EPA registration Pending

- **Pyrimidinols Class:**
  - Rubigan® - Fenarimol
Sterol Inhibitors

- Extremely broad spectrum
  - Summer patch
  - Anthracnose
  - Dollar Spot
  - Brown Patch
  - Take-all Patch
  - Leaf spots
  - Some snow molds
  - Some do well on fairy ring
Localized Penetrant Pythium Fungicides

- **Banol®:**
  - Carbamate : Propamocarb ; Membrane Biosynthesis

- **Subdue® MAXX:**
  - Phenylamide : Metalaxyl ; Interfere With Nucleic Acid Synthesis

- **Steller ® (State Reg. Pending, EPA Complete)**
  - Combines new chemistry (fluopicolide) with another acropetal penetrant (propamocarb-banol)
  - Fluopicolide belongs to the acylpicolides and is an acropetal penetrant which is distributed in xylem tissue – anti-sporulant activity
FUNGICIDE CLASSES

Benzamides

- Introduced into Turf Market in Early 1990’s

- Prostar® : Flutolanil

- Interferes With Cell Respiration in Mitochondria
Prostar® : Flutolanil

- Originally developed for the control of *Rhizoctonia* diseases (brown patch) on rice.
- Control of many basidiomycete fungi
  - Fairy ring, brown patch, red thread
Acropetal Penetrant Dollar Spot Only Fungicide

- Emerald (Boscalid)
  - Effective for two turf diseases
    - Bentgrass Dead Spot
    - Dollar spot
  - Effective at very low rates (0.13-0.18 oz/1000M)
Acropetal Penetrant Strobilurins

- Two materials
- Move upward in the xylem from
Acropetal Penetrant Strobilurins

- **Heritage®**: Azoxystrobin
- Introduced in 1997
- Works Better in Preventative Control; Low Use Rates
- Broad Spectrum of Control; 14 to 28 Day Residual Based on Rate
Acropetal Penetrant Strobilurins

- **Disarm®**: Fluoxastrobin
- Introduced in 2006
- Works Better in Preventative Control; Low Use Rates
- Broad Spectrum of Control; 14 to 28 Day Residual Based on Rate
Heritage and Disarm

- Good to excellent
  - Brown patch
  - Take-all patch
  - Red thread
  - Summer Patch
  - Some short term Pythium control
  - Dollar spot?
Review of Fungicide Classes

- Four Types
  - Contact
  - Localized Penetrant (LP)
  - Acropetal Penetrant (AP)
  - Systemic

Contacts-outside plant
LP- May move in outside leaf tissues
AP- Move upward from point of application

LOCK AND KEY-Fungicide binds to certain target of fungi
Managing Fungicide Resistance

- Documented Cases To date:
  - Dollar spot = DMI - thiophanate methyl-dicarboximides
  - Anthracnose = strobiluron - thiophanate methyl-DMI
  - Pink Snow Mold = dicarboximides
  - Gray Leaf Spot = strobiluron and maybe others?
  - Pythium Blight = strobiluron and mefenoxam
How Resistance May Happen

Natural Population

1 x

Fungi strain resistant to fungicide

Fungi susceptible to fungicide

2 x
FRAC

- Fungicide Resistance Action Committee Classification Scheme of Fungicides
- Uses numbers and letters to
- Helps to determine
  - 1.) risk or potential resistance issues
  - 2.) Help end users determine good tank mixes

Examples= FRAC Code M; FRAC Code 4- Subdue MAXX
Tank mixing, Pre mixes and Rotations

- Besides Cultural Practices and Preventive Applications-Remain the Best Method

Many ‘pre-mixed’ fungicides are currently on market
Any Questions?