FUNGICIDAS

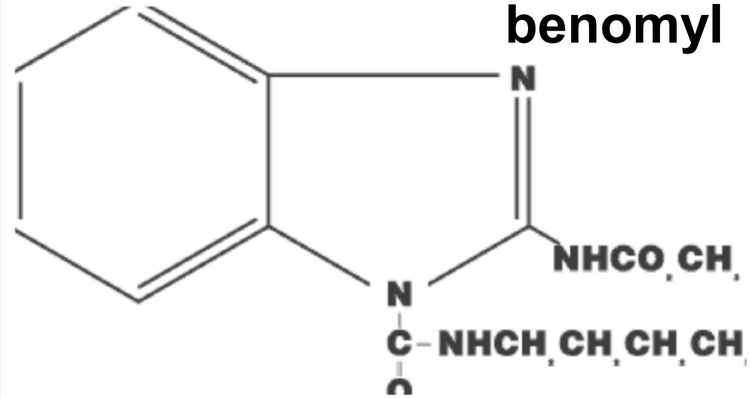
ERRADICANTES
PROTETORES
INORGÂNICOS
ORGÂNICOS
SISTÊMICOS
BENZIMIDAZÓIS

ESTÁ CORRETO?

Low volume over-the-row sprayer

Tratamento de feijão – 1906 (Cornell University)

benomyl



FUNGICIDAS – Critérios de classificação

SISTEMICIDADE, PRINCÍPIO GERAL DE CONTROLE, MODO DE AÇÃO, INGREDIENTE ATIVO...

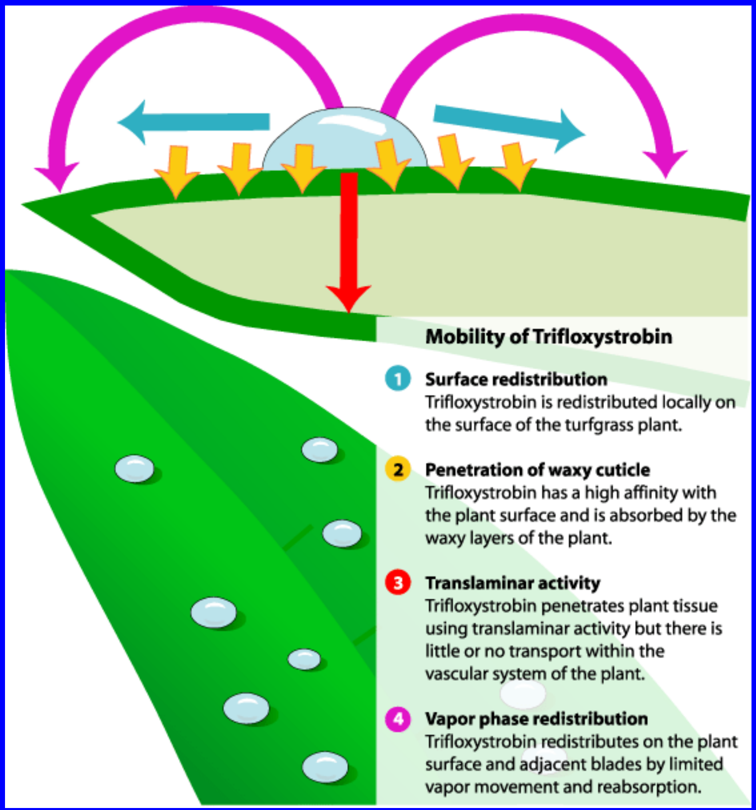
SISTEMICIDADE – Capacidade de translocar na planta

Sistêmico – translocação via vaso

Imóvel, tópico, residual, não sistêmico – não penetra a planta

Mesostêmico, translaminar, penetrante – atravessa ou move-se no limbo foliar

Exemplo de mobilidade mesostêmica (translaminar) de Trifloxistrobina



Vincelli, P. QoI (Strobilurin) Fungicides: Benefits and Risks
http://www.apsnet.org/edcenter/advanced/topics/Pages/StrobilurinFungicides.aspx

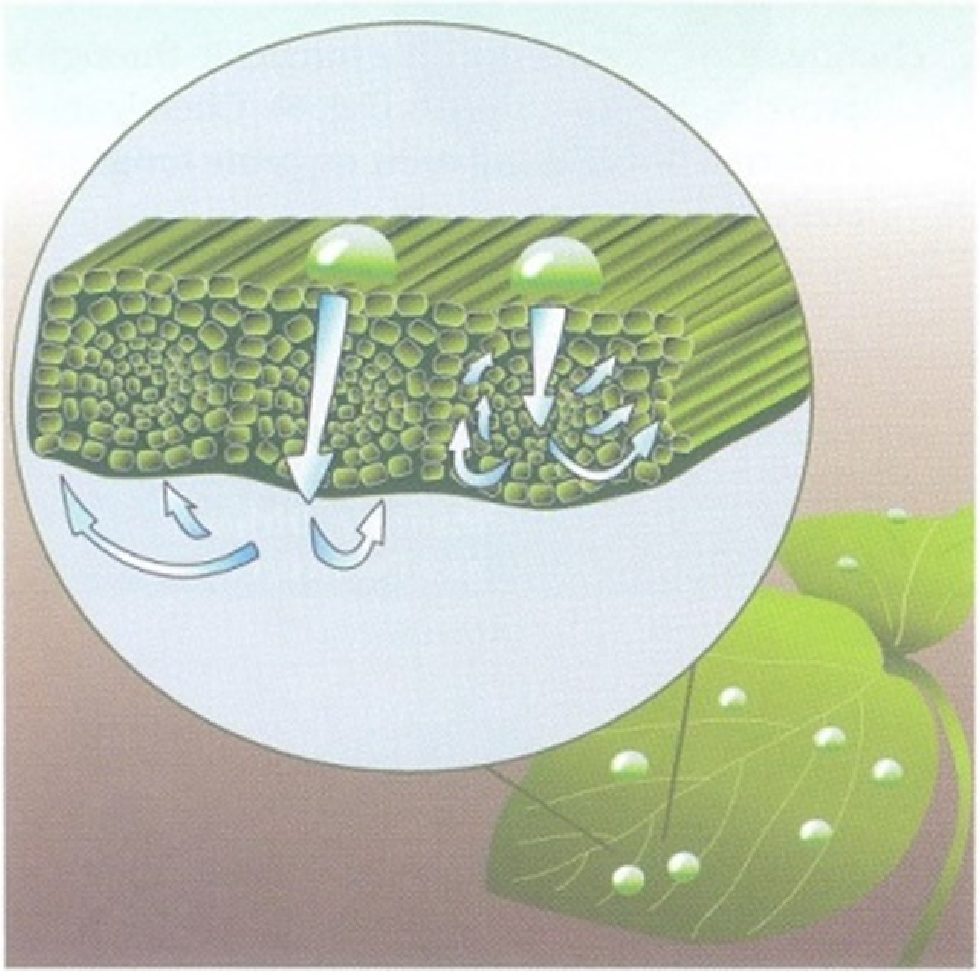
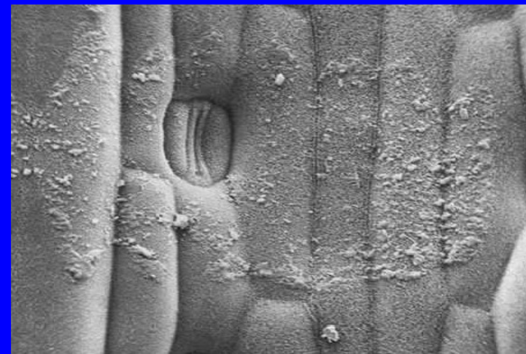
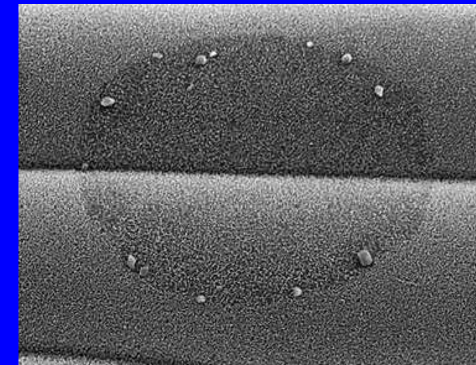


Fig. 6. Fungicides with systemic activity enter plant tissue and move within the plant (droplet on right); fungicides with translaminar activity move through the leaf from the sprayed surface to the nonsprayed surface (droplet on left). (Courtesy Iowa State University)

Muller et al. (2013)

SISTEMICIDADE





Aplicação do fungicida

Fungicida Imóvel

Fungicida translaminar

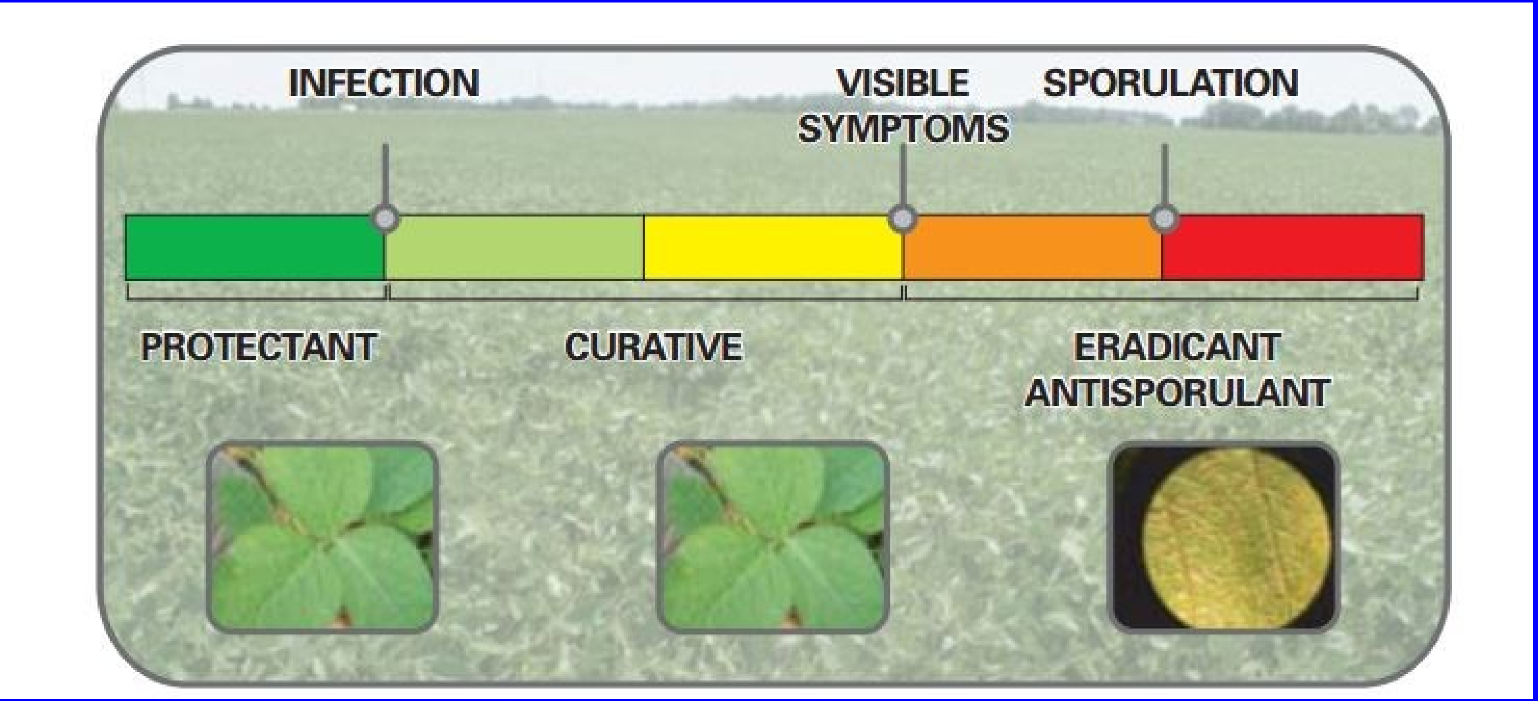
Fungicida sistêmico

Dorrance et al., 2007 (https://www.oardc.ohio-state.edu/soyrust/2007edition/fungisoyrust.pdf)

FUNGICIDAS – Critérios de classificação

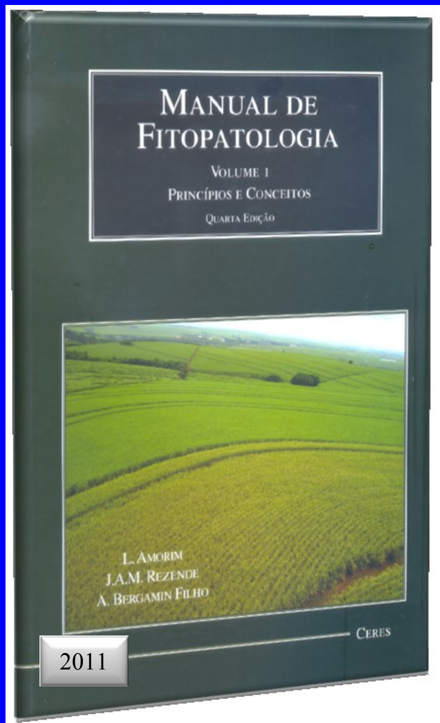
PRINCÍPIO GERAL DE CONTROLE

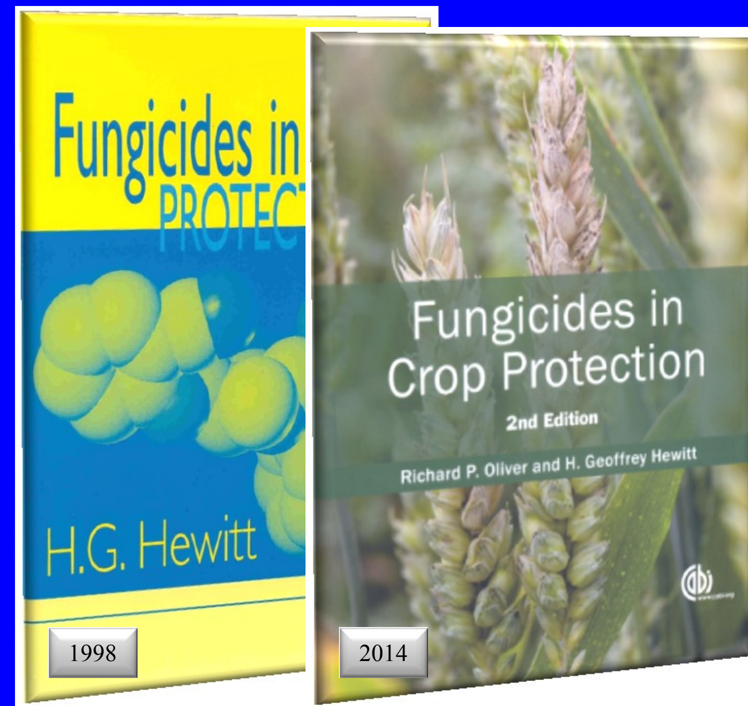
<u>Protetor</u> – impede a penetração
<u>Curativo</u> – impede a colonização (pós-penetração)
<u>Erradicante</u> – elimina o inóculo (na lesão, no solo...)



Dorrance et al., 2007 (https://www.oardc.ohio-state.edu/soyrust/2007edition/fungisoyrust.pdf)

FUNGICIDAS – Critérios de classificação





Movimentação & Princípio em que se fundamenta a aplicação

- **Imóveis**

✓ Erradicantes ou de contato
✓ Protetores ou residuais

- **Sistêmicos**

Diferentes critérios

- Mobilidade
- Subfases do processo infeccioso (Princípios de controle)
- Absorção pelos esporos (contato vs residual)
- **Modo de ação (*)**
- Grupo químico

Performance (Modo de ação - MOA *)
MOA ~ FRAC (2014)

- General disruption of cell function (1998)
  M - Multi-site (2014)

- Disruption of nuclear process (1988)
  Mitosis and Cell Division (2014)
  Cytoskeleton and motor proteins (FRAC)

MOA – Mode of Action

Reis et al. (2007)

- Organela celular afetada (membrana, mitocôndria, ribossomo...)

Oliver & Hewitt (2014)

- Wheter the product is a protectant, curtive or erradicant
- The broad biological function that is inhibited (respiration)
- Specific molecular target (Quinone oxidase)

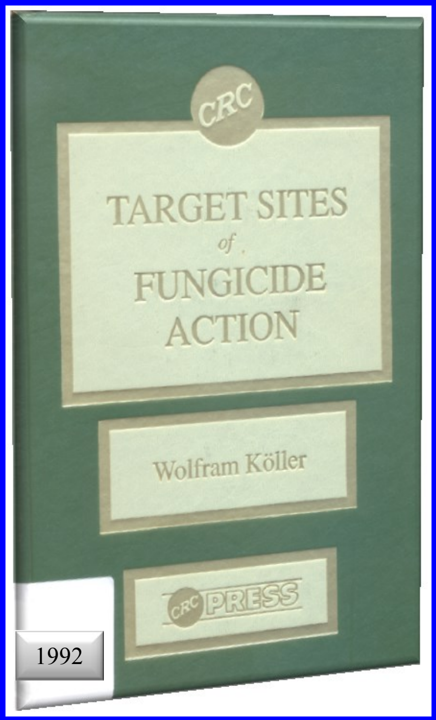
Mueller et al. (2013)

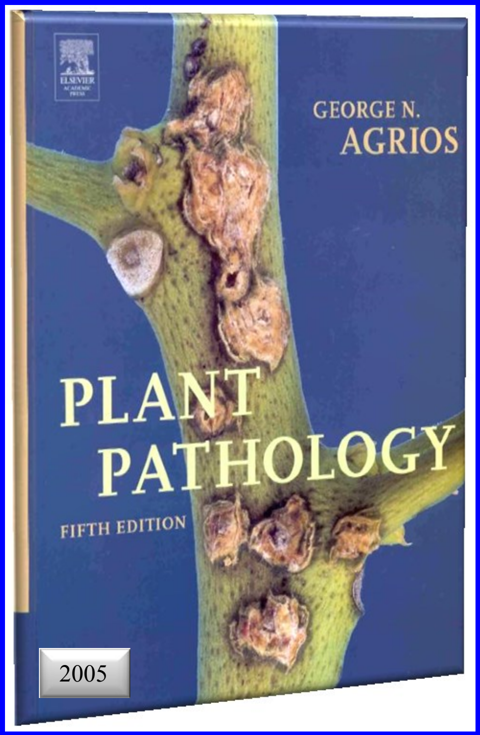
- Specific biochemical process targeted by the fungicide (cell membranes, respiration)

Van den Bosh et al. (2014)

- Specific molecular target (Quinone oxidase)

FUNGICIDAS – Critérios de classificação





Alvo do produto

•Target sites of carboxamides
•Target sites of tubulin-binding fungicides
•Target sites of fungicides to control oomycetes...

Types of chemicals

•**Inorganic chemicals**
•**Organic chemicals**
- ✓ Contact protetive fungicides
- ✓ Systemic fungicides
- ✓ Organophosphate fungicides...

...Antibiotics

Nome do ingrediente ativo

•22 ametocradin
•30 amisulbrom
•47 azaconazole
•54 azoxystrobin

•913 vinclozolin
•917 zineb

FUNGICIDAS

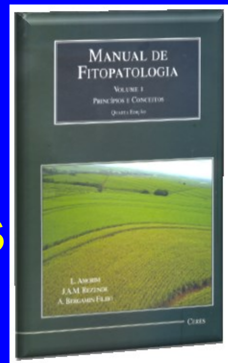
Fungicidas imóveis

INORGÂNICOS

ORGÂNICOS

Fungicidas sistêmicos

BENZIMIDAZÓIS



M - Multi-sítios

M1 – Cúpricos

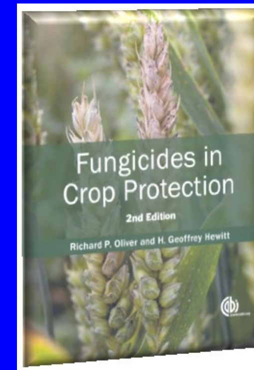
M2 – Enxofre

M3 – Ditiocarbamatos

B – Mitose

formação da tubulina

BENZIMIDAZÓIS



Tratamento de feijão – 1906 (Cornell University)

Low volume over-the-row sprayer

Fungicidas Multi-Sítios

CARACTERÍSTICAS

- Atividade erradicante ou protetora, nunca curativa
- Inibidores inespecíficos de reações bioquímicas, causando disfunção geral da célula
- Não sistêmicos, fitotóxicos

Aplicação de fumigante em campos de produção de morangos na Flórida, EUA

Fungicidas Multi-Sítios - erradicantes

Agem sobre o inóculo

Tratamento de sementes →
Tratamento de inverno →
Tratamento de solo ↓

Ácido sulfúrico (deslintamento de algodão)
Thiram e captan (imóveis)
★ Tiabendazol (sistêmico, erradicante, uni-sítio)

Calda sulfo-cálcica (no Brasil adubo sulfocal)
Calda bordalesa com elevada concentração de cobre

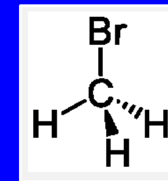
Voláteis (Fumigantes)
Biocidas (altamente tóxicos)
- Fungos
- Nematóides
- Insetos
- Plantas daninhas

Exigem cobertura impermeabilizante
Exigem intervalo pré-plantio
Brometo de metila, formol, dazomet...

Fungicidas Multi-Sítios - erradicantes

BROMETO DE METILA –

Gás incolor e inodoro (cloropicrina)
Biocida
França 1930 – rapidamente em todo o mundo
100 diferentes culturas
EUA – entre os 5 produtos mais usados (1994)
83 % desinfestação do solo (morango e hortícolas)
11 % pós-colheita ou commodities
6 % estrutural



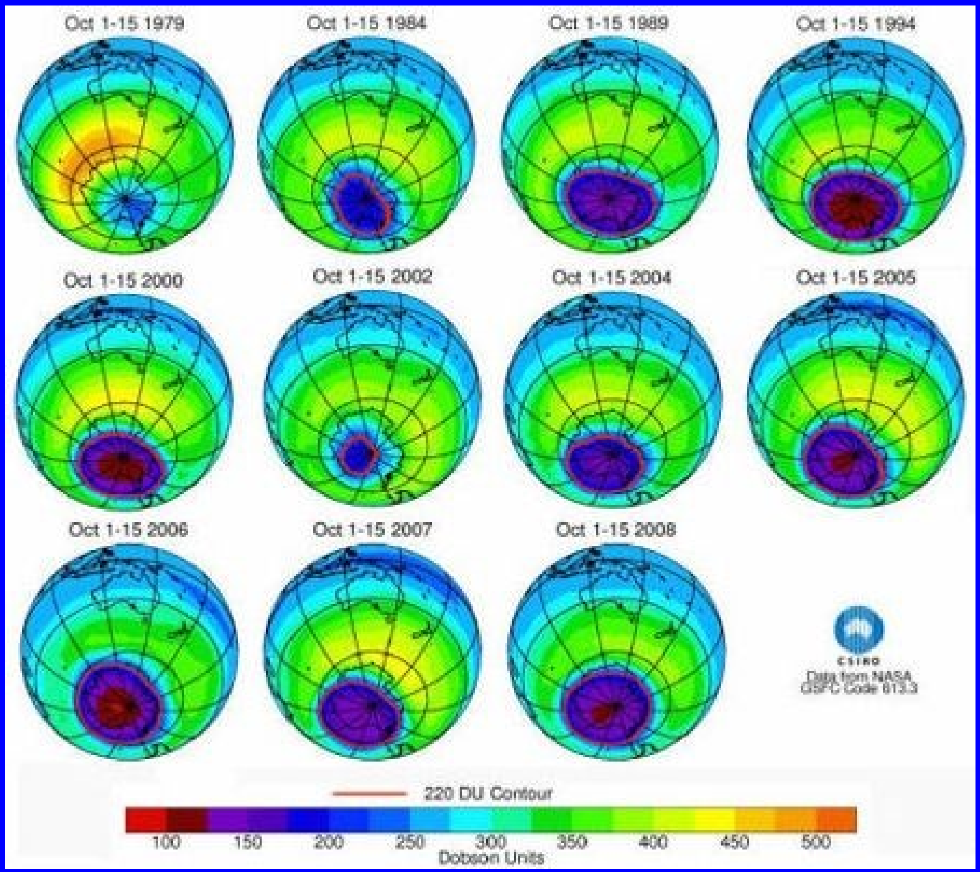
Até 1993 uso indiscriminado

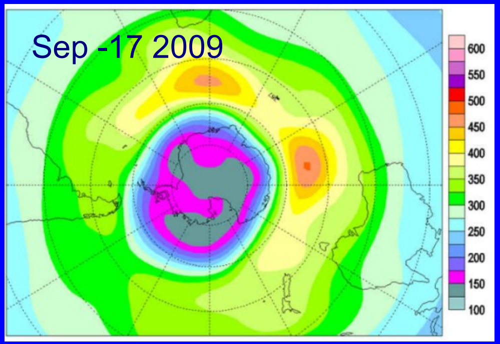
16/9/1987 - Montreal Protocol on Substances that Deplete the Ozone Layer
Brometo de metila incluído em 1992

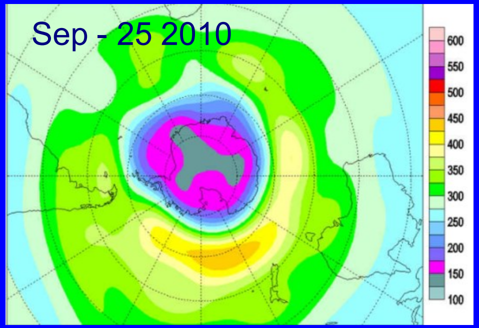
1993 - 1998 – consumo congelado (em relação a 1991)
1999 - 2000 – 25 % de redução
2001 - 2002 – 50 % de redução
2003 - 2004 – 70 % de redução
2005 - fim de uso (exceto casos especiais)

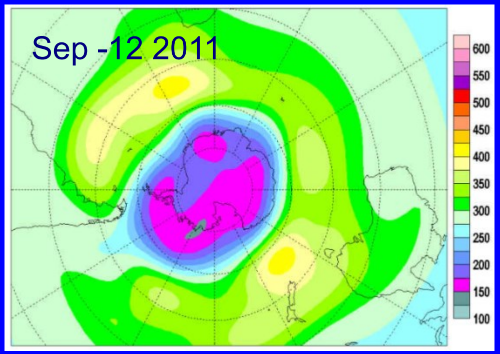
http://www.epa.gov/ozone/mbr/

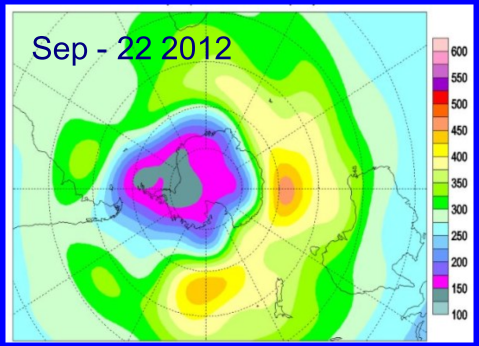
O buraco de ozônio na antártica

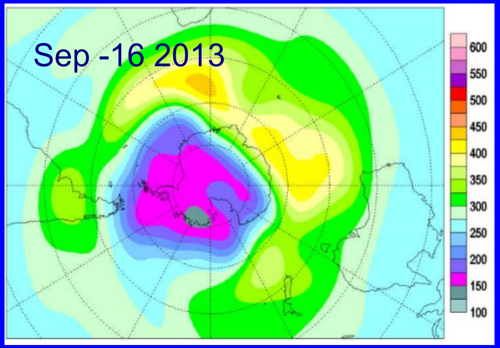


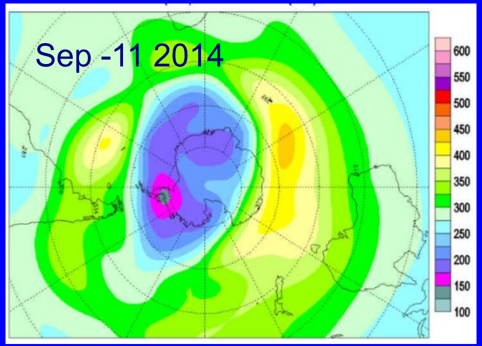






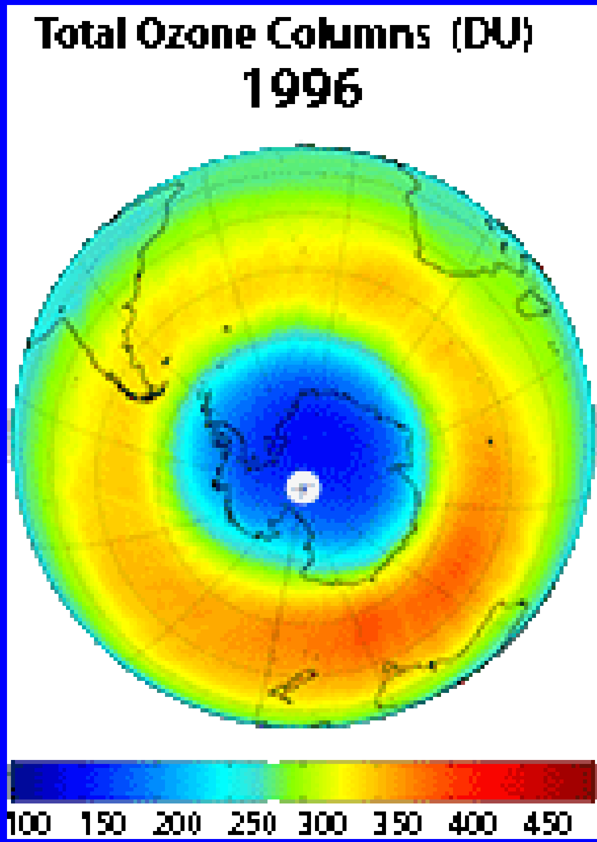


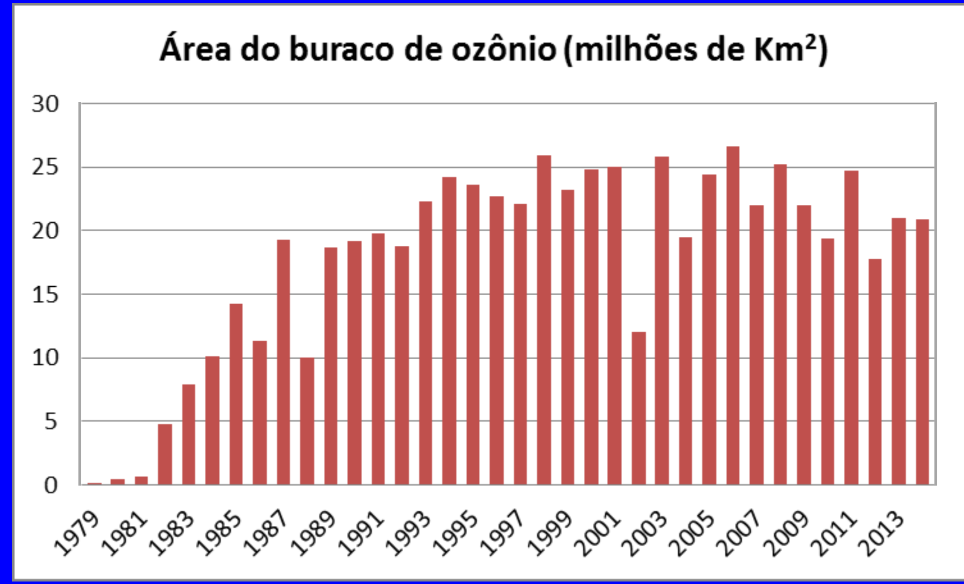


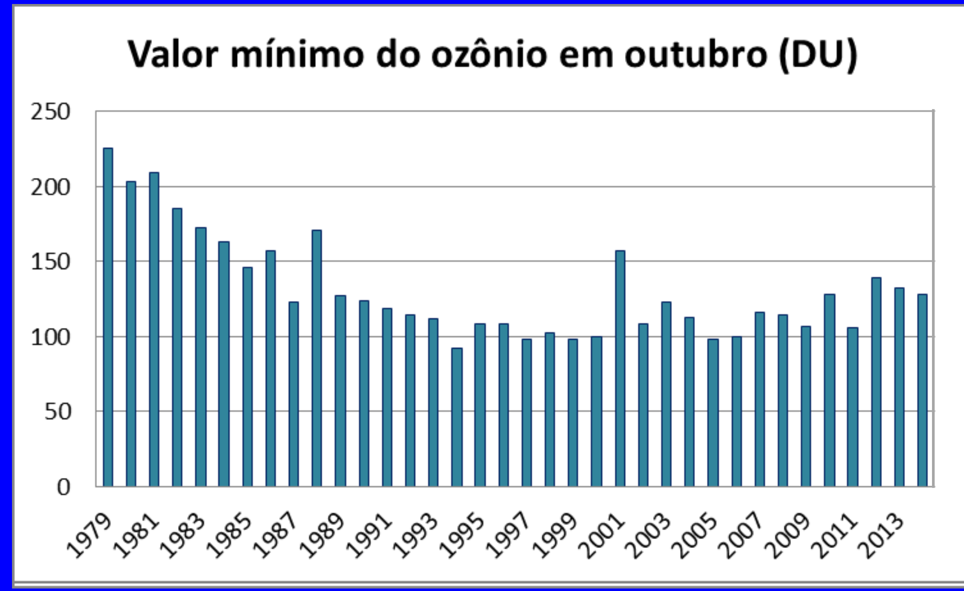


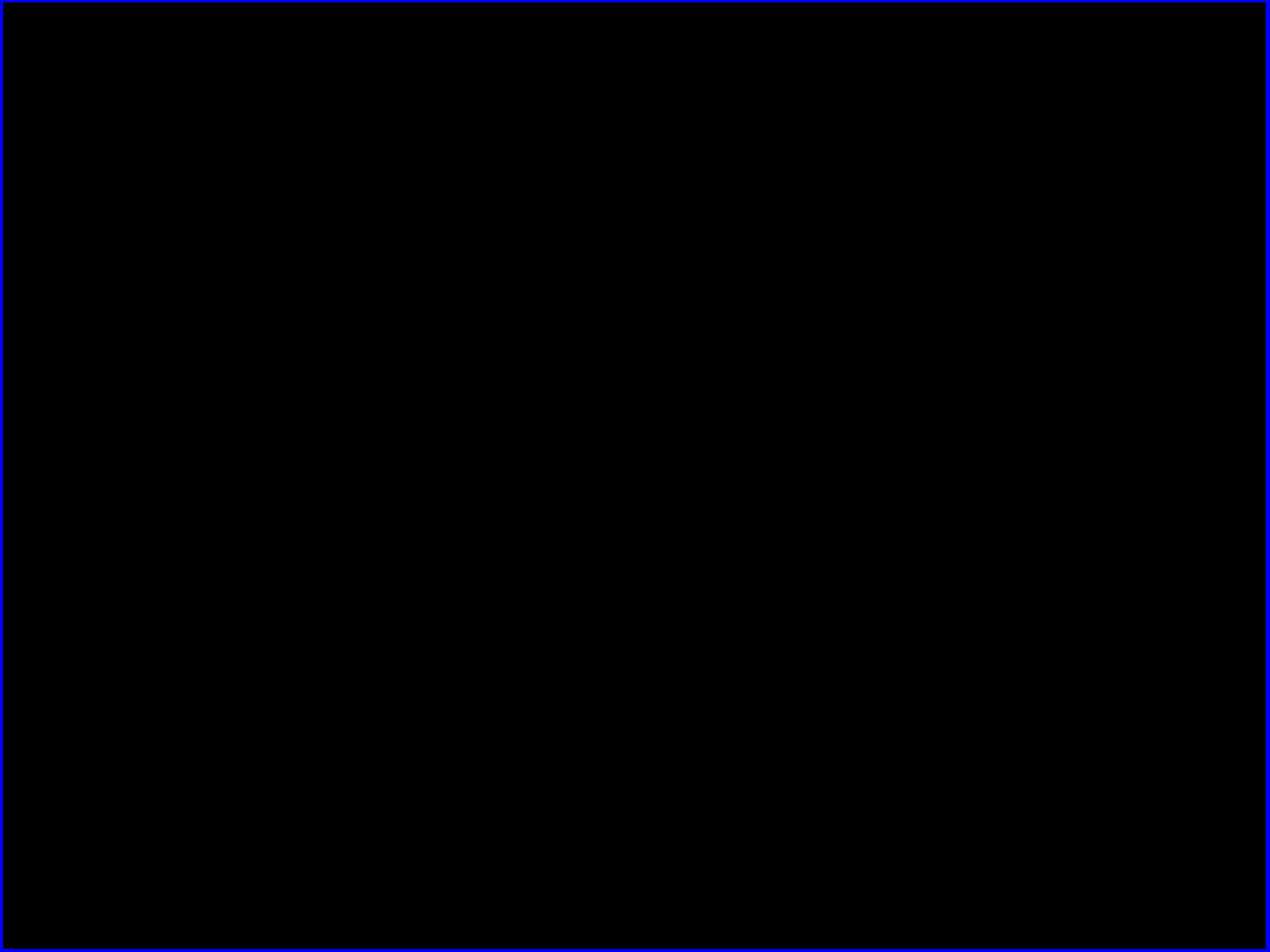
http://www.theozonehole.com/

O buraco de ozônio na antártica









Fungicidas Multi-Sítios - erradicantes

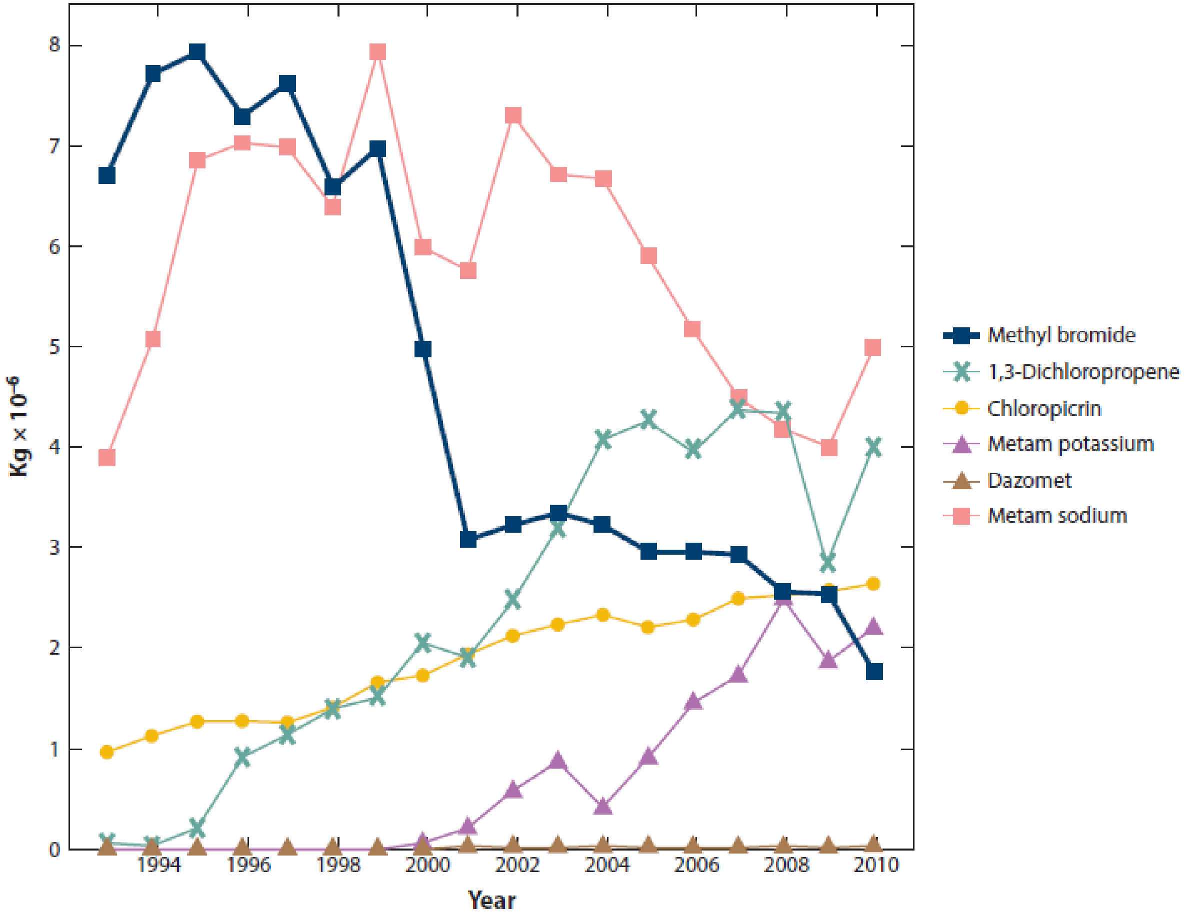


Figure 2

Mass in millions of kilograms of agricultural fumigants used in California fields between 1993 and 2010. These data show the mandated (partial) replacement of methyl bromide (*thicker dark blue line*) with 1,3-dichloropropene (*green Xs*), chloropicrin (*yellow circles*), metam potassium (potassium n-methyldithiocarbamate) (*purple triangles*), and dazomet (*brown triangles*); metam sodium (*pink squares*) has been used throughout the period. Data are from the California Pesticide Use Reports. The figure is modified with permission from Epstein & Zhang (42).

Epstein (2014)

Fungicidas Multi-Sítios – protetores

CARACTERÍSTICAS

- Atividade **protetora**, nunca curativa
- Inibidores inespecíficos de reações bioquímicas, causando disfunção geral da célula
- Não sistêmicos, fitotóxicos
- Insolúveis (pouco solúveis) em água
- Baixa fungitoxicidade inerente – doses elevadas

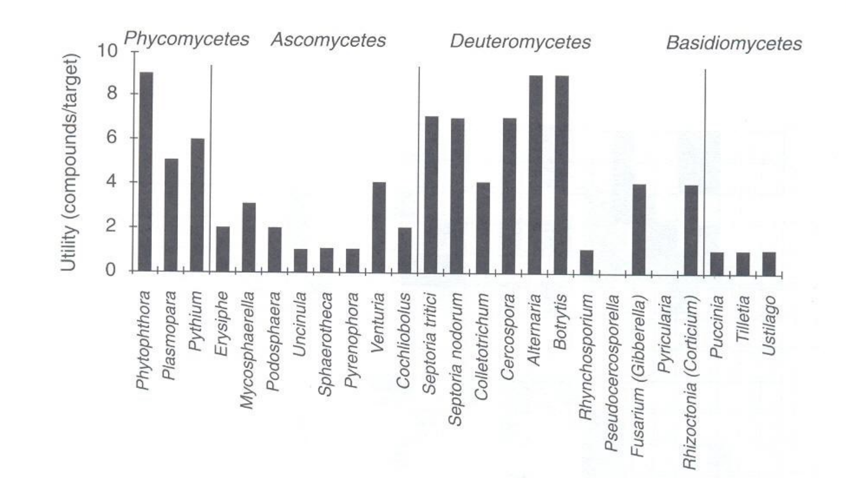


Fig. 4.2. Major use spectrum of general cell toxicants.

INORGÂNICOS

COBRE, ENXOFRE, BICARBONATO DE POTÁSSIO, MERCÚRIO

ORGÂNICOS

DITIOCARBAMATOS
DICARBOXIMIDAS
ORGANOESTÂNICOS

Fungicidas Multi-sítios

• Inorgânicos

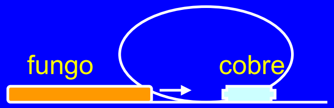
Cúpricos { Sulfato de cobre, oxicloreto de cobre, hidróxido de cobre, óxido cuproso, calda bordalesa

Cu^{+} e Cu^{2+} são prontamente assimilados por células fúngicas mas... FITOTÓXICOS

↓

Compostos insolúveis - **Como penetram os fungos?**

↓ Acidificação e dissolução de produtos

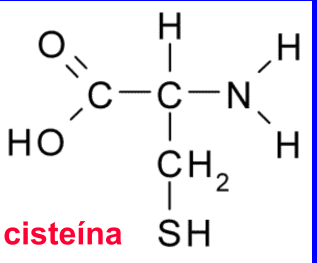


CO_2 da água da chuva
Excreções da planta
Exsudatos do fungo – aminoácidos e ácido málico (malato de Cu)

Como agem nos fungos?

• Cu^{+} e Cu^{2+} formam complexos com aminoácidos de enzimas com radicais SH. Em enzimas da membrana plasmática causam acúmulo de K^{+} nas células

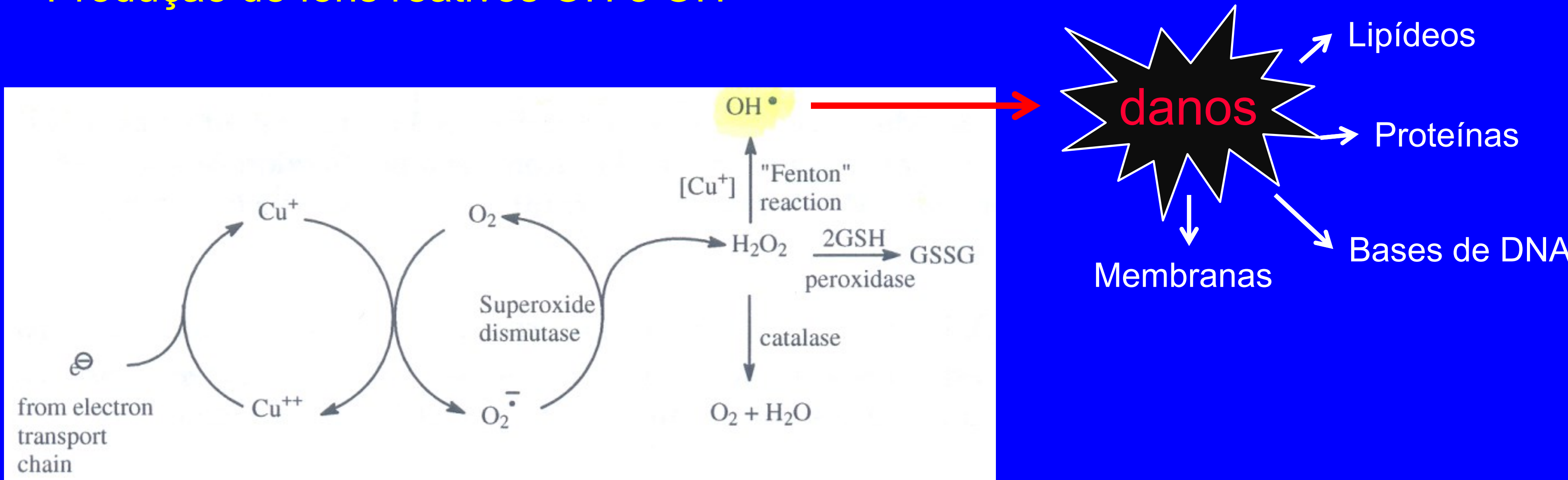
Breakdown of cell integrity



cisteína

Como agem nos fungos?

- Produção de íons reativos OH e OH^-



Lista de doenças controladas com fungicidas cúpricos em:

http://www.copper.org/applications/compounds/

Cúpricos inibem a respiração, interferem na integridade da membrana, mas depende do produto....(Montag et al., 2006)

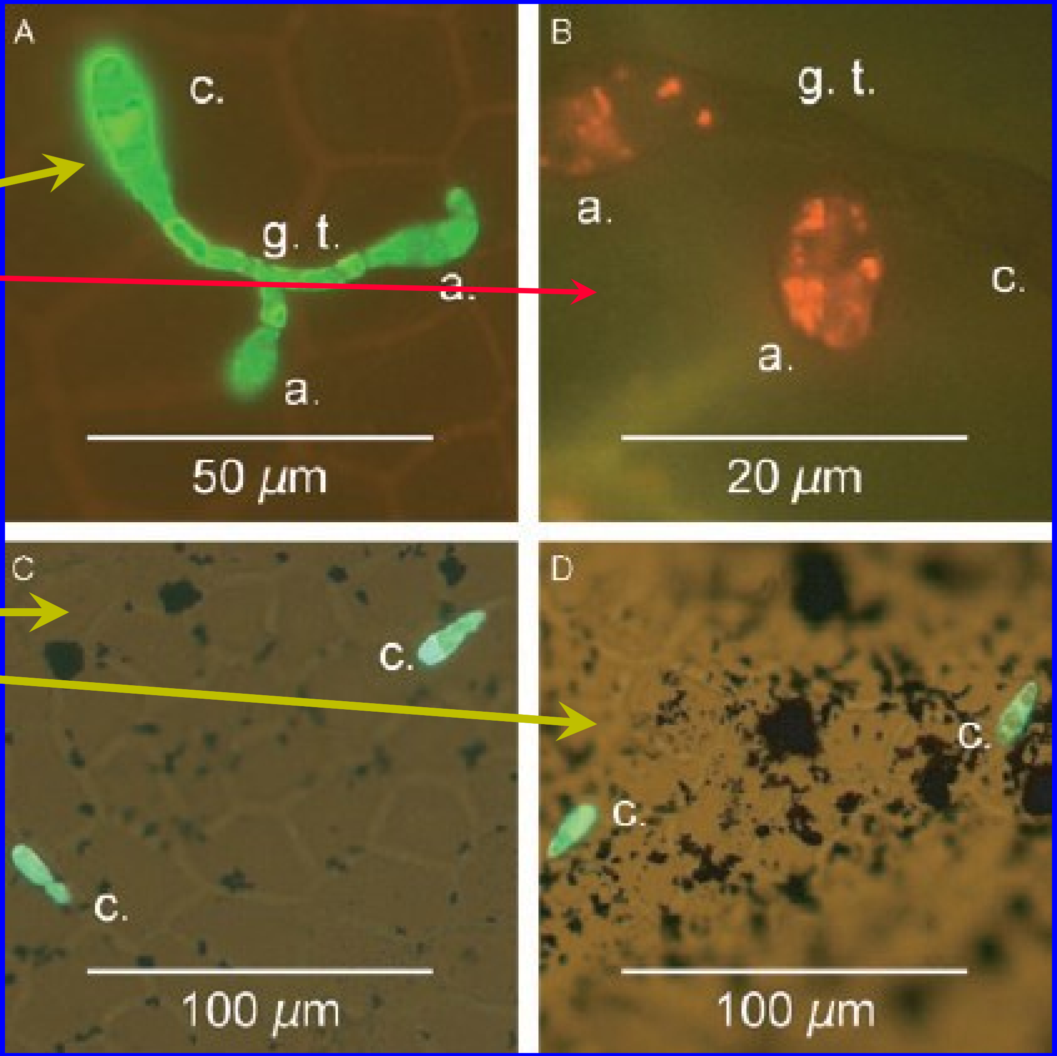
Montag *et al*. (2006) – sulfato de cobre, hidróxido de cobre e óxido de cobre

Effects of different copper compounds at various concentrations on germination and fluorescence of conidia of *Venturia inaequalis* on cuticular membranes (CM) of *Malus* × *domestica* cv. Gloster

Treatment	Ungerminated conidia (%)[a]	integridade FDA fluorescing conidia (%)[a]	respiração CTC fluorescing conidia (%)[a]
Control	11 (2.6)	89.0 (2.6)	86.3 (5.6)
$CuSO_4$ (mmol/l)			
1	100 (0)	0 (0)	0 (0)
10	100 (0)	0 (0)	0 (0)
25	100 (0)	0 (0)	0 (0)
$Cu(OH)_2$ (mmol/l)			
1	100 (0)	32.3 (4.9)	0 (0)
10	100 (0)	10.4 (3.5)	0 (0)
25	100 (0)	7.8 (3.0)	0 (0)
CuO (mmol/l)			
1	100 (0)	29.8 (7.2)	0 (0)
10	100 (0)	22.2 (5.3)	0 (0)
25	100 (0)	19.1 (5.8)	0 (0)

Copper treatments were applied 24 h before inoculation and allowed to dry. Inoculated CM were incubated for 24 h in sealed Petri dishes in a growth cabinet at 20°C in darkness. Effects were assessed microscopically using fluorescein diacetate (FDA) and cyanoditolyl tetrazolium chloride (CTC) as vital stains.

[a]Results are given in percentage of the total number of conidia. Two independent experiments were conducted, each consisting of 10 replicates per treatment, resulting in 20 observations per treatment. Values are given as mean (SD).



Fungicidas multi-sítios

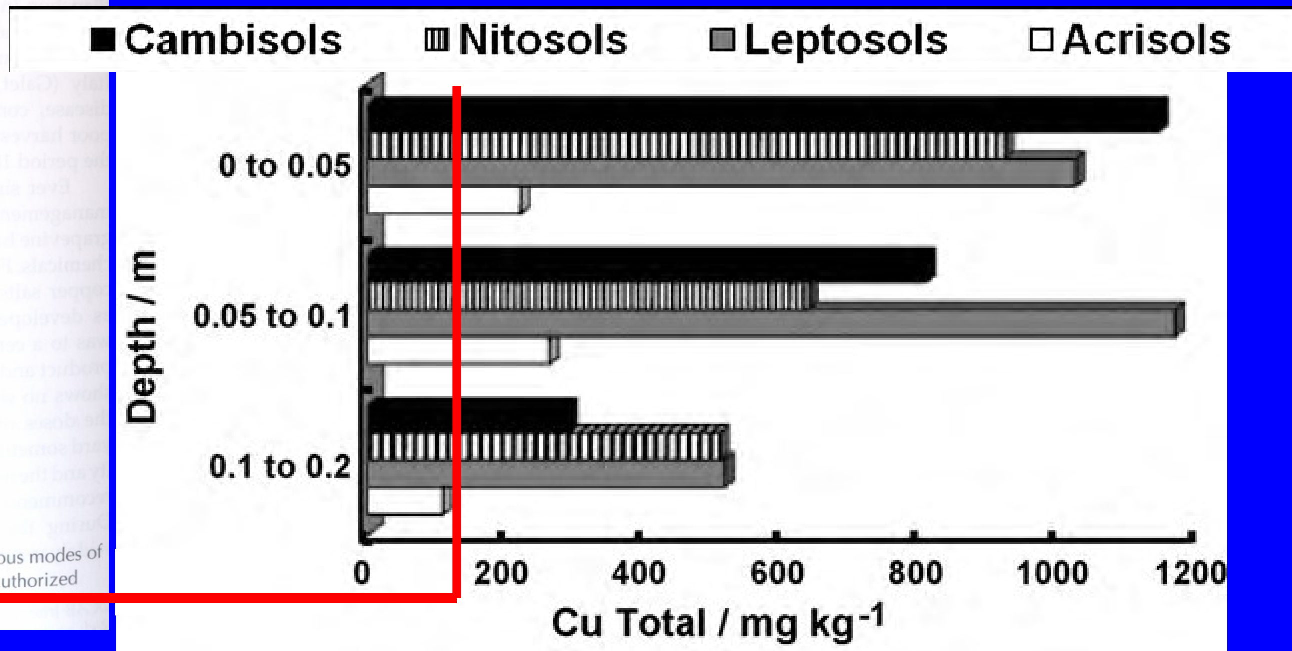
Vantagens dos Cúpricos

Baixo custo (depende do mercado)
Amplo espectro (inclusive bactérias)
Sem relatos de resistência (bactérias)
Uso em agricultura orgânica
Uso em tratamentos de inverno

Resíduos no solo

Vinhedos (26)
RS, com histórico de aplicação de Calda bordalesa

Limite de resíduo
140 mg kg $^{-1}$



Nogueirol et al. (2010)

Remediação de solos contaminados com cobre

K.A. Mackie et al. / Environmental Pollution 167 (2012) 16–26

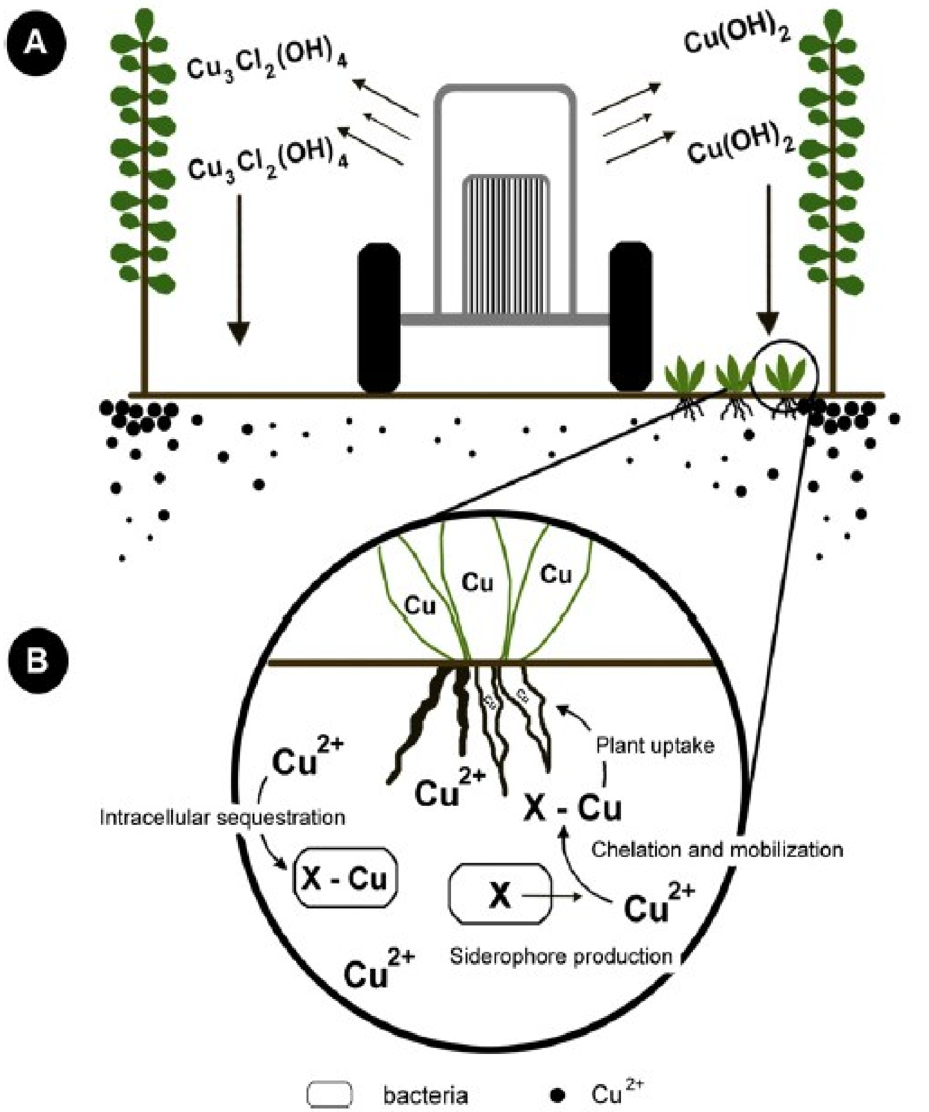


Table 2
Plants selected for copper removal around world.

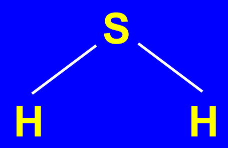
Location	Experiment type	Soil type and origin	Plant	Approach	Copper accumulated in shoots mg kg^{-1}	Copper accumulated in roots mg kg^{-1}	Source
Europe							
Hérault, S. France	Greenhouse pot experiment	Calcareous sandstone-slate and alluvial deposits	*Zea mays* cv. Gaucho	No addition	7.14–17.2	23.4–584	(Brun et al., 2001)
Hérault, S. France	Field	Calcareous sandstone-slate and alluvial deposits	Wild species	No addition;			(Brun et al., 1998)
				Dactylis glomerata	3.54–12.2	–	
				Poa annua	10.9–11.4	–	
				Andryala integrifolia	9.44–26.6	4.56–18.00	
				Hypochoeris radicata	8.48–21.6	7.40–16.5	
				Senecio vulgaris	14.7–19.8	14.9–28.3	
				Sanguisorba minor	9.01–11.3	9.81–13.1	
				Rumex acetosella	9.78–32.7	–	
				Allium polyanthum	3.80–10.2	–	
				Rubia peregrina	4.53–16.0	–	
Roujan, France	Pot experiment	Variable soil samples	*Lycopersicon esculentum* cv. St Pierre	No addition	4.1–13.9	19–189	(Chaignon et al., 2003)
Portugal	Greenhouse pot experiment	$CuSO_4$ amended soil	*Brassica juncea*	Addition of microorganisms; *Achromobacter xylosoxidans*	~2–8	~30–180	(Ma et al., 2009)
Serbia	Outdoor pot experiment	Clay loam/Vineyard	*Brassica napus*	Addition of Chelators;			(Zeremski-Škorić et al., 2010)
				EDDS	38.6–316.4	78.1–244.4	
				EDTA	34.2–52.0	202.1–390.6	
Slovenia	Soil column experiment	Sandy loam/Vineyard	*Brassica rapa*	Addition of Chelators;			(Kos and Leštan, 2004)
				Citric acid	11.28		
				EDDS	37.81		
				DTPA	24.28		
				EDTA	21.71		
Spain	Soil and plant collection from 15 sites	Malachite outcrops	+32 species	No addition;			(Poschenrieder et al., 2001)
				Sedum sediforme	406	639	
				Hirschfeldia incana	355	97	
				Hyparrhenia hirta	10	202	
				Brachypodium retusum	34	124	
				Echium vulgare	32	99	
				Foeniculum vulgare	16	51	
				Alyssum maritimum	25	30	
				Psoralea bituminosa	11	32	
United Kingdom, Chile, China	Greenhouse pot experiment	Factory and mine tailings		No addition;			(Song et al., 2004)
			Silene vulgaris	*Silene vulgaris*	0.77[a]	0.75[a]	
			Elsholtzia splendens	*Elsholtzia splendens*	0.60[a]	0.74[a]	
South America							
Brazil	Greenhouse pot experiment	Inceptisol and Mollisol/ Vineyard	*Avena sativa*	Addition of microorganisms;			(Andreazza et al., 2010a)
				Pseudomonas putida A1	~1150–1200 mg kg^{-1}		
				Stenotrophomonas maltophilia A2	~1100–1200 mg kg^{-1}		
				Acinetobacter calcoaeticus A6	~1100–1300 mg kg^{-1}		
Asia							
Zhejian Province, China	Greenhouse pot experiment	Alluvial sandy loam/ Agriculture	*Elsholtzia splendens*	Addition of Chelators;			(Chen et al., 2006)
				Glucose	~85	~440	
				Citric acid	~75	~400	
Zhejian Province, China	Greenhouse pot experiment	Alluvial sandy loam/ Agriculture	*Trifolium repens*	Addition of Chelators;			(Chen et al., 2006)
				Glucose	~50	~320	
				Citric acid	~25	~360	

Fungicidas multi-sítios

- **Inorgânicos**

  sulfúricos (enxofre)

Foi o primeiro fungicida utilizado na prática e muito
popular até os ditiocarbamatos (orgânicos com S como captan e thiram)
1971 - o mais usado nos EUA

Inibem respiração – sulfeto de hidrogênio 
Quelatos com metais pesados dentro das células dos fungos

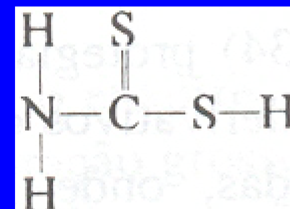
Enxofre elementar (S^0) – oídios e ácaros (seletividade por absorção)
fitotóxico em cucurbitáceas (temperaturas elevadas)
baixa toxicidade ao homem / oomicetos / zigomicetos / insetos benéficos
boa opção em misturas com sistêmicos

Reconhecido como fitoalexina em 4 famílias botânicas contra patógenos vasculares (xilema). Williams & Cooper (2004)

Fungicidas multi-sítios

- **Orgânicos (1930)**
  - ditiocarbamatos e etilenobisditiocarbamatos

Compostos derivados do *ácido ditiocarbâmico*



Inativam o grupo –SH de aminoácidos

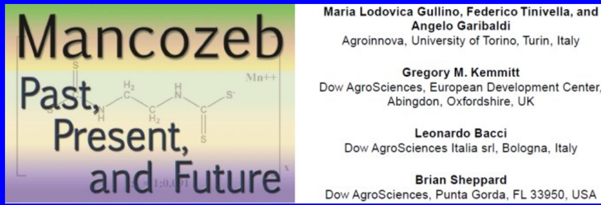
Eficientes a doses mais baixas que os inorgânicos, maior atividade residua

Degradados por microrganismos do solo sem deixar me

$(CH_3)_2N.CS.S$ $S.CS.N(CH_3)_2$	ziram	
$[-SCS.NHCH_2CH_2NHCS.S$ $]_x$	zineb	(1945)
$[(CH_3)_2NCS.S]_2$ $SCS.N(CH_3)_2$	ferbam	
$(CH_3)_2N.CS$ $CS.N(CH_3)_2$	thiram	(1934)
$[-SCS.NHCH_2CH_2NHCS.S$ $-]_x$	maneb	(1950)
$[-SCS.NHCH_2CH_2NHCS.S$ $-]_x$ $_y$	mancozeb	(1962)

Amplo espect
Baixo cu
Baixa toxicidade a s
Ampla aceitação

Mobilidade no solo
Persistência no alimento



Mancozeb + água → ethylene bisisothiocyanete sulfide (EBIS)

EBIS $\xrightarrow{UV}$ ethylene bisisothiocyanete (EBI) → Tóxicos (SH)

Plant Disease 2010 94: 1076-1087

Table 2. Effectiveness (%) of mancozeb applied alone for the control of key pathogens on different crops

Phylum/ Kingdom	Pathogen	Crop	Dose (g a.i./ha)	Effectiveness (%)[a]
Oomycetes	*Peronospora destructor*	Onion (*Allium cepa* L.)	400-5,600	50 ± 32
	Albugo cruciferarum	Mustard (*Brassica juncea* L.)	2,000	83
	Peronospora parasitica	Rocket (*Eruca sativa* L.)	1,280	97
	Pseudoperonospora cubensis	Melon (*Cucumis melo* L.)	1,600	62 ± 21
	Pseudoperonospora cubensis	Cucumber (*Cucumis sativus* L.)	1,600	50 ± 2
	Pseudoperonospora cubensis	Luffa vine (*Luffa acutangula* L.)	1,125-2,500	53 ± 18
	Phytophthora cactorum	Apple (*Malus* spp.)	2,240	60 ± 17
	Phytophthora fragariae	Strawberry (*Fragaria* × *ananassa*)	4,000-8,000	46 ± 31
	Bremia lactucae	Lettuce (*Lactuca sativa* L.)	1,440-1,600	52 ± 41
	Phytophthora vignae	Chick-pea (*Cicer arietinum* L.)	1,440	50
	Phytophthora infestans	Potato (*Solanum tuberosum* L.)	1,360-3,000	73 ± 22
	Phytophthora infestans	Tomato (*Solanum lycopersicum* L.)	2,500-3,000	61 ± 26
	Plasmopara viticola	Vine (*Vitis vinifera* L.)	800-3,600	79 ± 22
	Peronospora belbahrii	Basil (*Ocimum basilicum* L.)	1,600	54 ± 10
	Peronospora sparsa	Rose (*Rosa* spp.)	1,440	11
Ascomycetes	*Guignardia citricarpa*	Orange (*Citrus sinensis* L.)	1,600-2,400	64 ± 30
	Claviceps africana	Sorghum (*Sorghum vulgare* L.)	1,500	68
	Podosphaera xanthii	Watermelon (*Citrullus lanatus* Thunb.)	2,550	41 ± 14
	Didymella bryoniae	Watermelon	2,520	33 ± 31
	Didymella bryoniae	Melon	1,400	87 ± 10
	Taphrina deformans	Peach (*Prunus persica* L.)	1,600-2,500	75 ± 16
	Venturia inaequalis	Apple	2,500-5,200	66 ± 20
	Gloeodes pomigena and *Zygophiala jamaicensis*	Apple	3,554	67
	Botryosphaeria obtusa	Apple	3,554	40
	Aureobasidium pullulans	Pear (*Pyrus* spp.)	3,400	47 ± 21
	Microdochium panattoniana	Lettuce	500-1,400	65 ± 39
	Mycosphaerella arachidis	Peanut (*Arachis hypogaea* L.)	2,000	46
	Heterosporium echinulatum	Carnation (*Dianthus* spp.)	1,600	73 ± 27
Deuteromycetes	*Alternaria* spp.	Tangelo (*Citrus tangelo*, *C. reticulata* Blanco × *C. paradisi* Macf.)	1,600	93 ± 4
	Botrytis spp.	Onion	2,240	68
	Alternaria porri	Onion	2,500	44 ± 19
	Stemphylium vesicarium	Onion	2,500	52 ± 27
	Alternaria porri	Leek (*Allium porrum* L.)	2,500	95
	Stemphylium vesicarium	Asparagus (*Asparagus officinalis* L.)	1,700	88 ± 5
	Alternaria brassicae	Mustard	2,000	39 ± 11
	Alternaria brassicae	Cabbage (*Brassica oleracea* L.)	2,000	50 ± 27
	Alternaria dauci	Carrot (*Daucus carota* L.)	2,000	38 ± 17
	Septoria apiicola	Celery (*Apium graveolens* L.)	1,600	88 ± 13
	Septoria spp.	Wheat (*Triticum aestivum* L.)	1,500-1,600	58 ± 46
	Fusarium graminearum	Wheat	1,680	18 ± 5
	Bipolaris oryzae	Rice (*Oryza* spp.)	1,120	21

[a] Expressed as Abbot's index: (Control index – treatment index)/control index.

Table 2. (*continued from previous page*)

Phylum/ Kingdom	Pathogen	Crop	Dose (g a.i./ha)	Effectiveness (%)[a]
	Pyricularia oryzae	Rice	1,400	28
	Exserohilum turcicum	Corn (*Zea mays* L.)	1,300-1,680	93
	Cercospora zeae-maydis	Corn	1,260	31 ± 8
	Colletotrichum spp.	Sorghum	2,000	40
	Colletotrichum spp.	Apple	3,554	40
	Alternaria mali	Apple	3,360	15
	Alternaria spp. and *Stemphylium* spp.	Pear	3,200	63 ± 30
	Colletotrichum acutatum	Strawberry	1,600	21 (with yield increase)
	Cercospora arachidicola	Peanut	2,400	93 ± 1
	Rhizoctonia solani	Soybean (*Glycine max* L.)	1,600	57 ± 10
	Ascochyta rabiei	Chick-pea	1,600-1,700	20 ± 9
	Alternaria alternata	Olive (*Olea europea* L.)	1,944	86
	Alternaria solani	Potato	1,600-2,400	36 ± 20
	Fusarium oxysporum f. sp. *lycopersici*	Tomato	2,520	54
	Septoria lycopersici	Tomato	1,600-2,000	40 ± 15
	Alternaria solani	Tomato	1,600-2,000	43 ± 20
	Colletotrichum coccodes	Tomato	1,680-2,500	57 ± 21
	Phomopsis viticola	Vine	1,920-3,600	73 ± 20
	Gloeosporium ampelophagum	Vine	2,400	51 ± 18
	Rhizoctonia solani	Rosemary (*Rosmarinus officinalis* L.)	1,800	71 ± 20
	Botrytis cinerea	Rose	1,600	35
	Botrytis cinerea	Geranium (*Pelargonium zonale*)	500	50 ± 10
	Botrytis elliptica	Iris (*Iris* spp.)	1,350	90
	Colletotrichum gloeosporioides	Anemone (*Anemone* spp.)	1,600	45
	Colletotrichum gloeosporioides	Euonymus (*Euonymus fortunei*)	1,400	42
	Septoria cornicola	Red osier dogwood (*Cornus sericea* L.)	1,440	82 ± 15
	Colletotrichum acutatum	Azalea (*Azalea japonica* L.)	1,440	95 ± 5
Basidiomycetes	*Puccinia allii*	Garlic (*Allium sativum* L.)	1,600	65
	Puccinia asparagi	Asparagus	1,400	49
	Puccinia triticina	Wheat	700-2,800	81 ± 9
	Puccinia striiformis	Barley (*Hordeum vulgare* L.)	1,600	50 ± 3
	Puccinia sorghi	Corn	1,680	24
	Puccinia sorghi	Sorghum	1,260-2,000	52 ± 27
	Tranzschelia discolor	Peach	2,000	76
	Tranzschelia discolor	Plum (*Prunus domestica* L.)	1,600	73 ± 18
	Uromyces viciae-fabae	Pea (*Pisum sativum* L.)	1,000-1,500	58 ± 2
	Uromyces appendiculatus	Bean (*Phaseolus vulgaris* L.)	1,600	60
	Puccinia arachidis	Peanut	2,000-2,400	49 ± 12
	Uromyces viciae-fabae	Faba bean (*Vicia faba* L.)	800-1,360	57 ± 26
	Puccinia hemerocallis	Daylily (*Hemerocallis* spp.)	1,440	95
	Puccinia horiana	Chrysanthemum (*Chrysanthemum* spp.)	1,400-1,600	45 ± 15
	Uredo spp.	Daisy (*Dendranthema frutescens*)	1,600	85 ± 15
	Puccinia pelargonii-zonalis	Geranium	564	95
	Uromyces caryophyllinus	Carnation	2,000	50 ± 18
Bacteria	*Pseudomonas syringae*	Melon	1,575	59
	Xanthomonas campestris pv. *cucurbitae*	Cucumber	1,600	33 ± 4
	Xanthomonas vesicatoria	Pepper (*Capsicum annuum* L.)	720-1,800	63 ± 1

SISTEMICIDADE

via apoplasto – xilema
via simplasto – floema (fosetil - caso único)

Absorção pelas raízes
- adesão a partículas de solo
- lixiviação

$\}$ **(*Kd* = [ ] fungicida no solo / [ ] na água)**

Absorção pelas folhas
- via não adaptada à absorção de nutriente
- adesão à cera epicuticular

Quantificação - Balanço lipofílico-hidrofílico
Coeficiente de partição octanol-água (log P, log K_{ow})

0 - 3

hidrofílico ← → **lipofílico**

SISTEMICIDADE

Absorção radicular

Produtos e coeficientes de partição

Active ingredient[a]	*Class*	*log* K_{ow}
Aclonifen (H)	Diphenyl-ether	3·98
Carbendazim (F)	Benzimidazole	1·37[d]
Dimethoate (I)	Organophosphate	0·77
Fenoxaprop (H)	Phenoxy	0·003[d]
Imazethapyr (H)	Imidazolinone	1·7[e]
Linuron (H)	Urea	3·0
Penconazole (F)	Triazole	3·6
Simazine (H)	Triazine	1·93

[a] H = herbicide, F = fungicide, I = insecticide.
[b] See text for measurement procedure.
[c] Of the conjugate acid.
[d] Measured at pH = 7.
[e] From Reference 31.

Sicbaldi et al., 1997. Pestic. Sci. 50:111-119

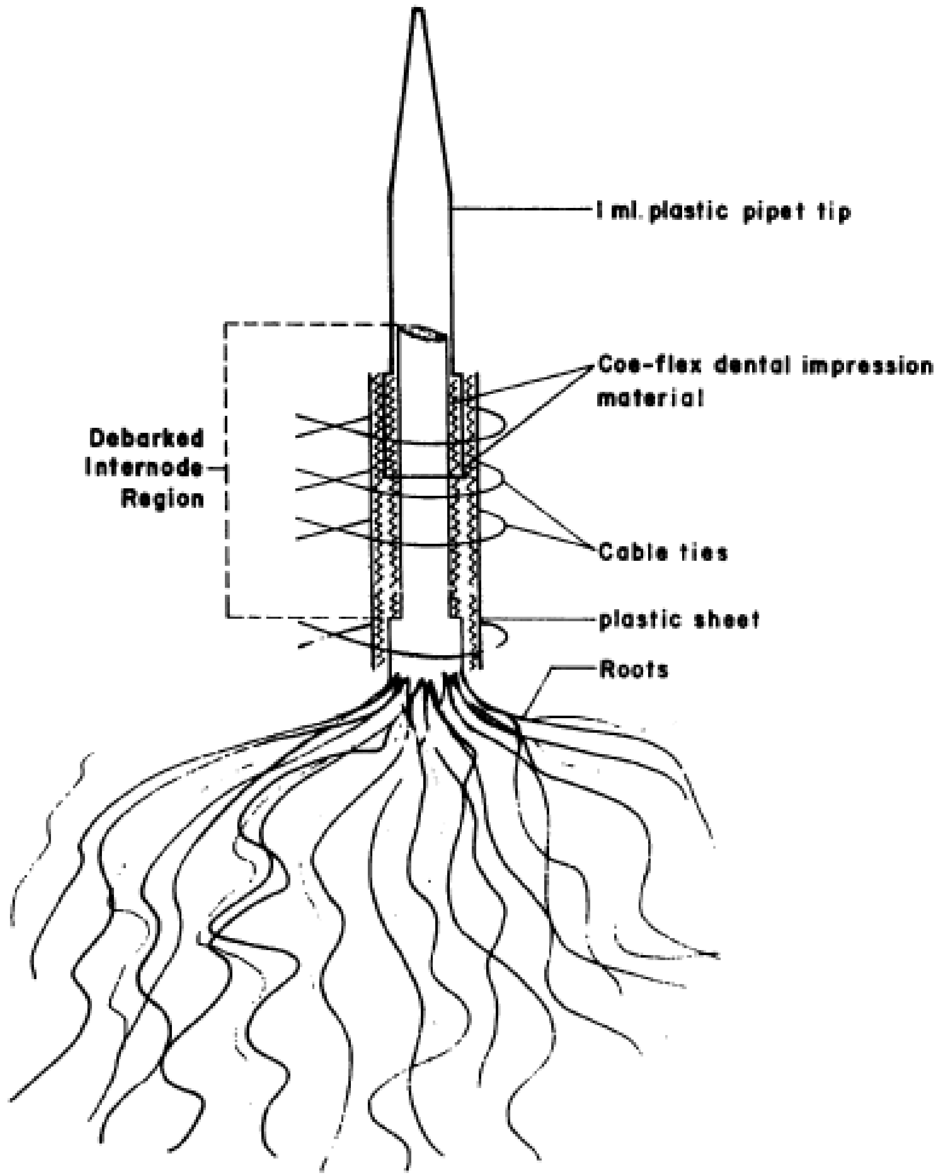


Figure 1. Diagram of soybean root-pipet tip assembly for pressure chamber.

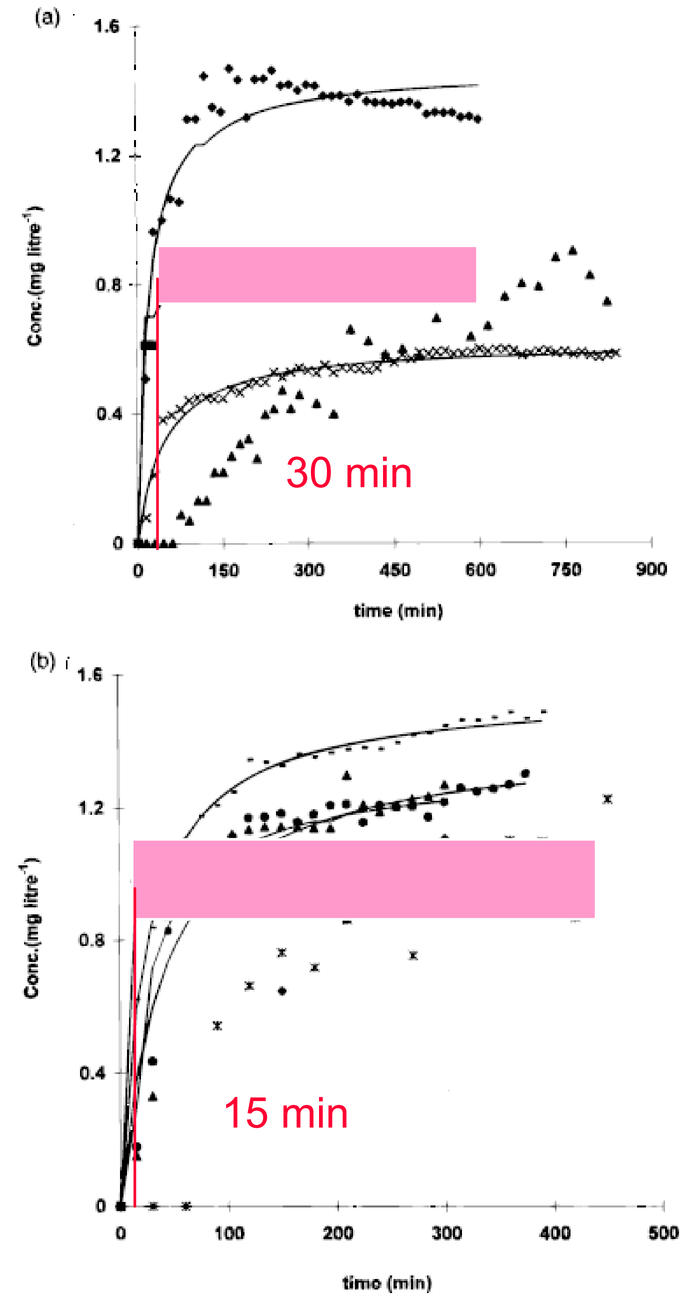


Fig. 2. Pesticides in xylem sap. (a) (◆) MBC, (▲) aclonifen, (×) fenoxaprop. (b) (◆) dimethoate, (▲) simazine, (★) penconazole, , (—) linuron.

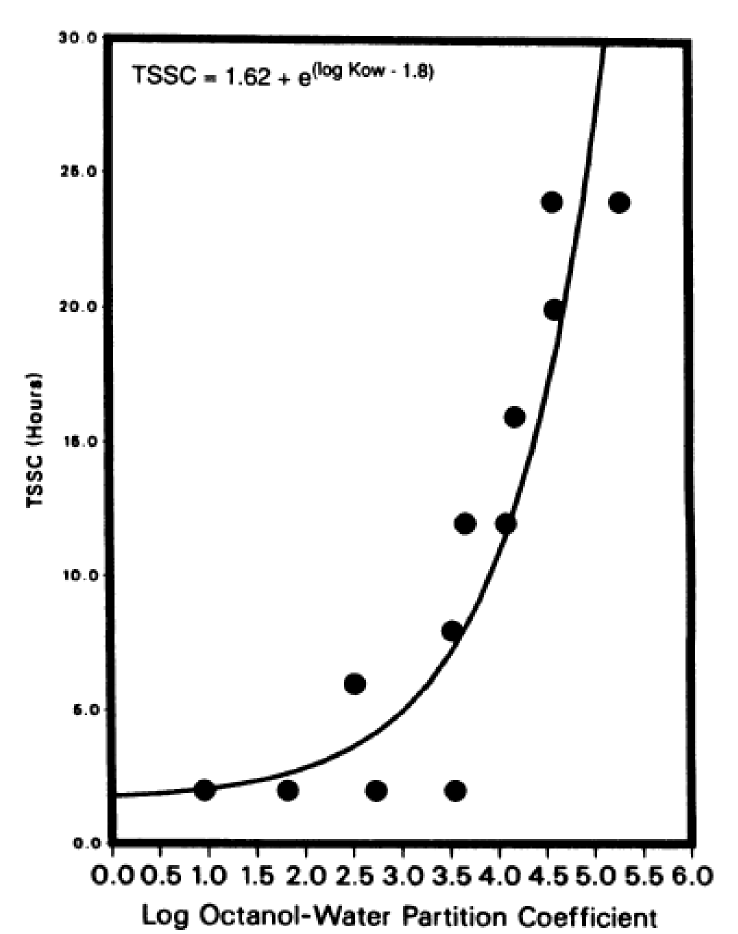


Figure 5. Relationship between time to steady-state concentration (TSSC) and compounds' log Kow values.

Hsu et al., 1993. Plant Physiol. 90:1573-8

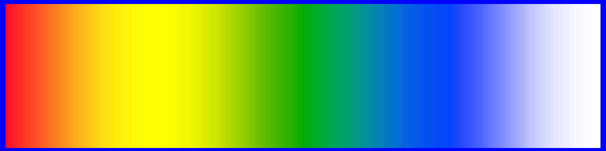
Sicbaldi et al., 1997. Pestic. Sci. 50:111-119

FUNGICIDAS SISTÊMICOS

CARACTERÍSTICAS

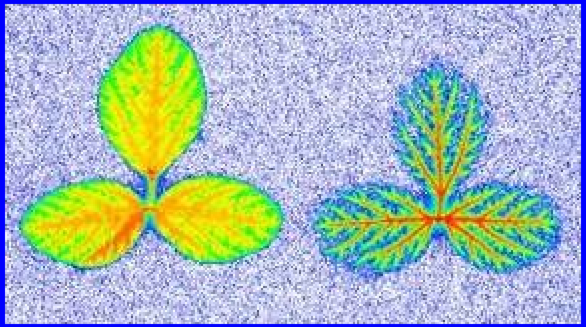
- Atividade protetora, curativa, imunizante ou erradicante
- Inibidores específicos de reações bioquímicas
- Elevada fungitoxicidade inerente – doses baixas
- Baixa fitotoxicidade
- Espectro de ação antifúngica variável
- Translocação acropétala via xilema (grande maioria)
- Menor acúmulo em áreas de baixa transpiração (frutos e folhas jovens) – acúmulo nos bordos foliares

Concentração de radioatividade do C14

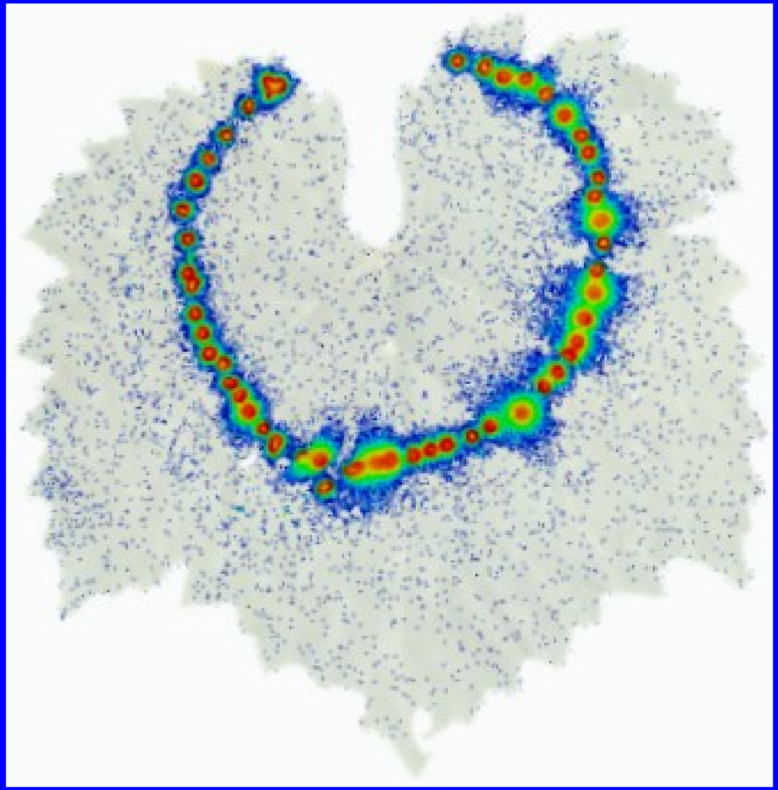


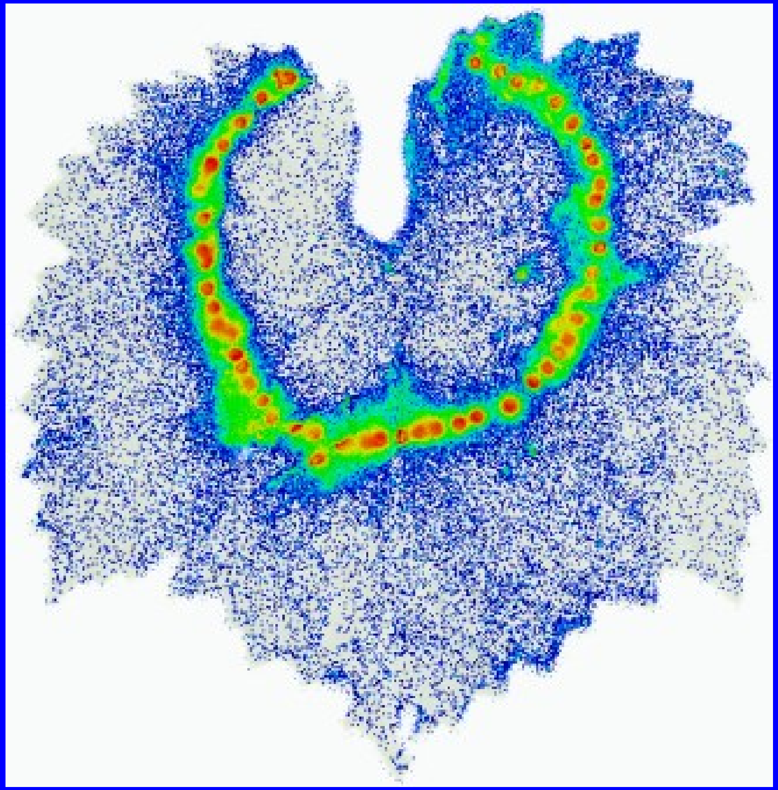
High *Low*

Por exemplo …..

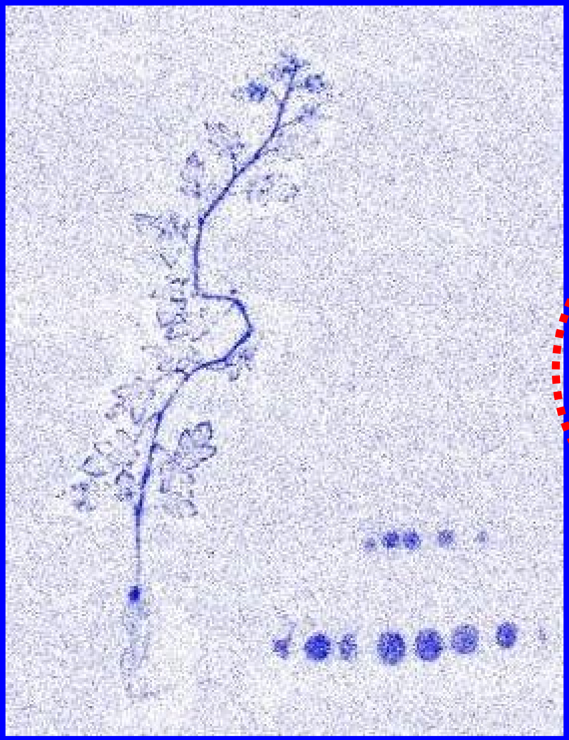


Fungicida não sistêmico - 7 e 14 dias após aplicação

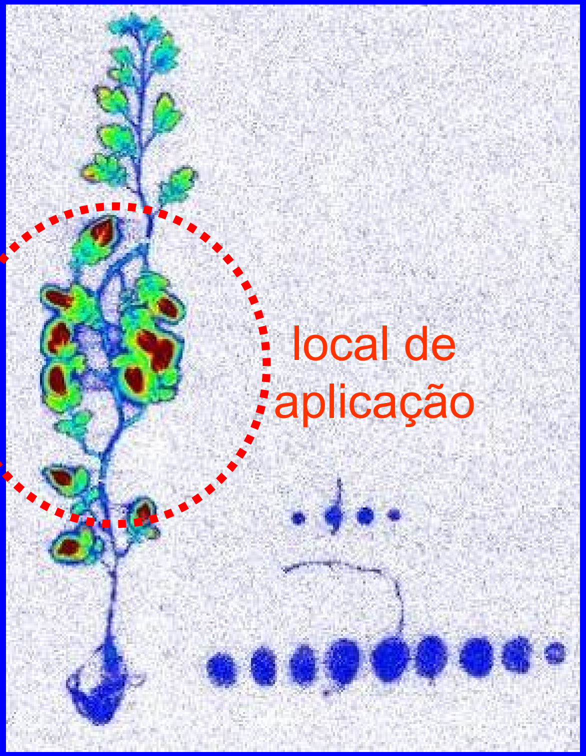




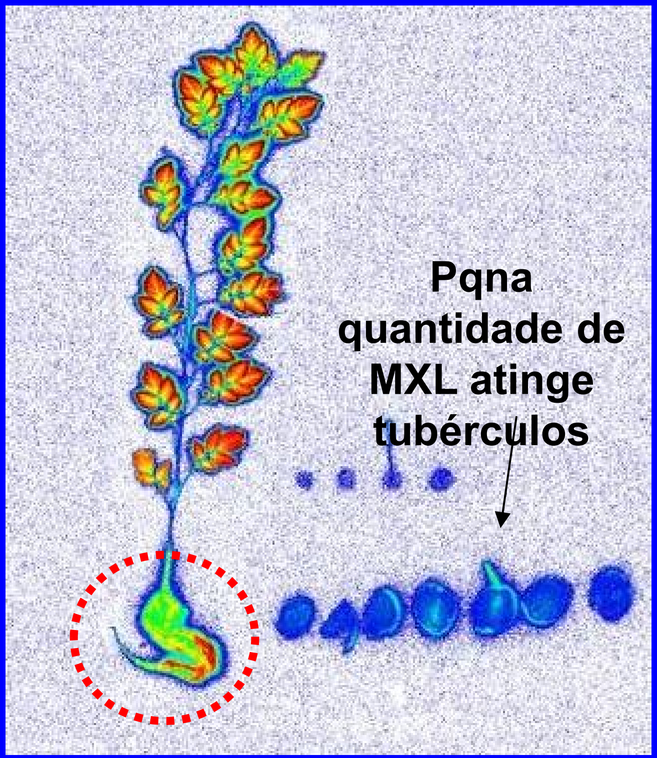
Movimento de metalaxyl em plantas e tubérculos de batata



Testemunha não tratada

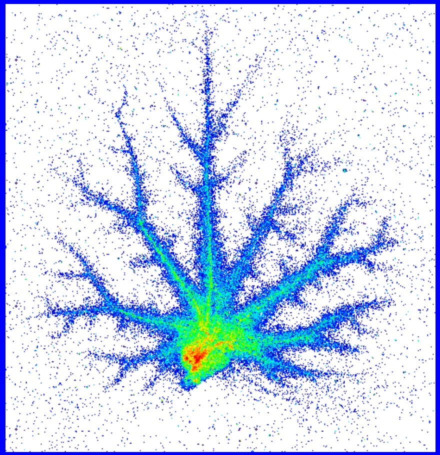


<u>Tratamento foliar:</u> **MXL com elevada concentração na área tratada e baixa acima dela e nenhuma abaixo**

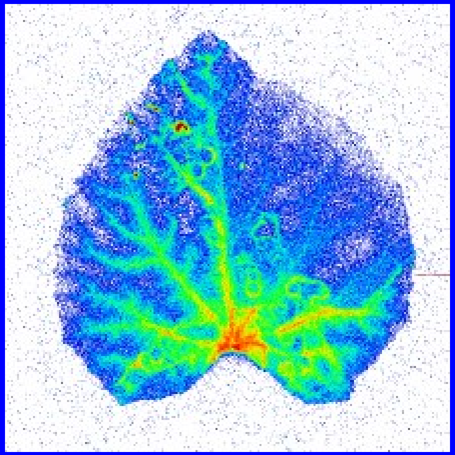


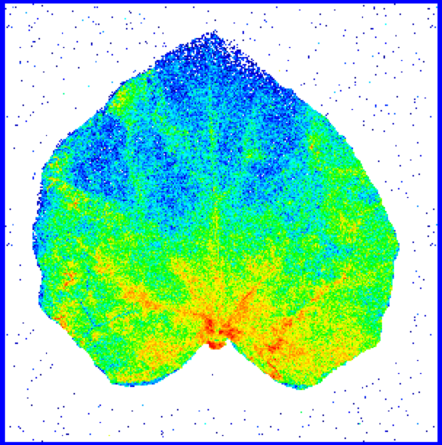
<u>Tratamento via solo:</u> MXL move-se das raízes para folhas

APLICAÇÃO NO PECÍOLO

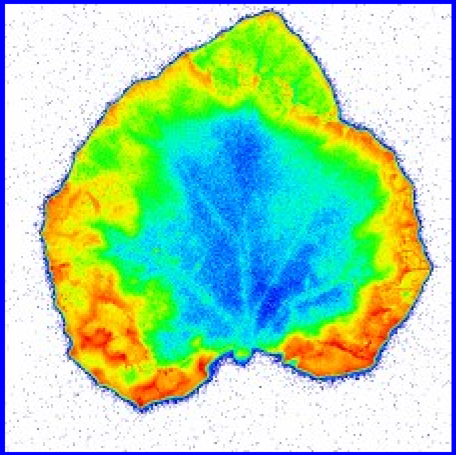


Azoxystrobin





Metalaxyl



1 dia **6 dias**

Derosal (Bayer)
carbendazim

DISFUNÇÃO NA MITOSE

BIOSSÍNTESE DA TUBULINA

BENZIMIDAZÓIS

Sistêmicos mais antigos (60)

	FRAC	AGROFIT
Benomyl - Fora do mercado Carbendazim Fuberidazole - Sem registro no Brasil Tiabendazol	benzimidazóis	benzimidazol
Tiofanato metílico	tiofanatos	precursor de benzimidazol

Tecto SC (Syngenta)
tiabendazol

Cerconil PM (Ihara)
Tiofanato metílico

Benzimidazois registrados no Brasil

Carbendazim – algodão, arroz, ☼citros☼, feijoeiro, macieira, milho, soja, trigo

Agroben, Apollo, Bavistin, Bendazol, Carben, Carbendazim, Carbomax, Change, Concreto, Czar, Delsene, Derosal, Derox, Fungicarb, Hexin, Impact, Imperadorbr, Lead, Locker, Mandarim, Minx, Novazin, Portero, Prevent, Proteat, Rivax, Rodazim, Streak, Tebuzim, Visrtuoso

Tiabendazol – algodão, abacaxi, arroz, banana, batata citros, coco, ervilha, feijão-vagem, girassol, gladíolo, maçã, mamão, maracujá, melão, milho, pimentão, soja

Tecto – tiabendazol (principalmente pós-colheita)
Cruiser Advanced – tabendazol, fludioxonil, metalaxil (tratamento de sementes)
Maxim Advanced – tabendazol, fludioxonil, metalaxil (tratamento de sementes)

Tiofanato metílico – abacaxi, abóbora, alho, amendoim, antúrio, arroz, banana, begônia, berinjela, café, cebola, citros, cravo, crisântemo, ervilha, feijão, gladíolo, hortênsia, maçã, mamão, manga, melancia, melão, morango, orquídea, pepino, quiabo, rosa, seringueira, soja, tomate, trigo, uva

Acronis, Apice, Brisa, Capo, Celeiro, Cercobin, Cerconil, Certeza, Dithiobin, Estrela, Flanco, Fieira, Fungiscan, Impact, Metiltofan, Mofotil, Pomme, Spring, Standak, Support, Tidy, Tiofanato-metílico, Tiofanil, Topsin, Treasure, Vincitore, Viper

Pathogens and crops targeted by benzimidazole fungicides in New Zealand

Pathogen	Disease	Crops
Botrytis cinerea[1]	Grey mould	Beans, berryfruit, grapes
Botrytis elliptica[1]	Blossom rot	Tomatoes, onions
Botrytis spp.	Various	Ornamentals
Sphaerotheca fuligena[1]	Powdery mildew	Cucurbits
Erysiphe cichoracearum[1]	Powdery mildew	Cucurbits
Monilinia fructicola[1]	Brown rot	Stonefruit
Monilinia laxa	Brown spot	Stonefruit
Mycosphaerella brassicicola[1]	Ring spot	Brassicas
Mycosphaerella fragariae[1]	Leaf spot	Strawberries
Penicillium digitatum[1]	Green mould	Citrus
Penicillium italicum	Blue mould	Citrus
Podosphaera leucotricha	Powdery mildew	Apples
Pseudocercosporella herpotrichoides[1]	Eyespot	Cereals
Rhynchosporium secalis	Scald	Barley
Sclerotinia spp.	Sclerotinia	Beans, lettuce, tobacco, tomatoes,
Septoria tritici	Speckled leaf blotch	Wheat
Venturia inaequalis[1], *Venturia pirina*	Black spot	Apples, pears
Botrysphaeria parva	Fruit rot	Avocadoes
Phomopsis sp.	Stem end rot	Avocadoes
Rhizoctonia spp.	Brown patch	Turf
Septoria apiicola[1]	Celery leaf spot	Celery

[1]Diseases for which resistant strains have been identified in New Zealand.

Beresford, RM. Benzimidazole management strategy. 2004 (http://resistance.nzpps.org/index.php?p=fungicides/benzimidazole)

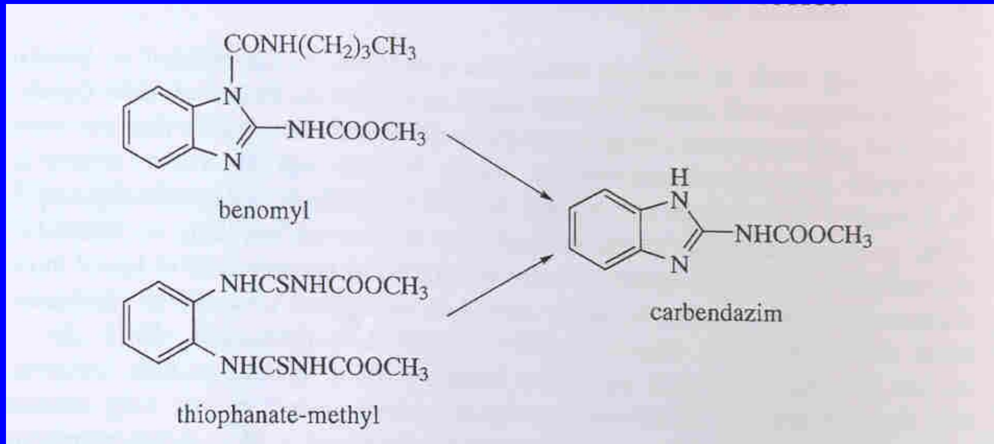
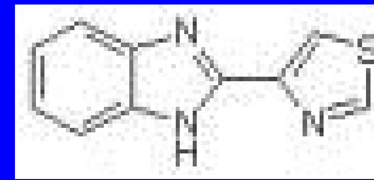
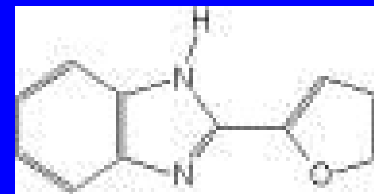


Figure 2 Conversions of benomyl and of thiophanate-methyl to a common product, carbendazim

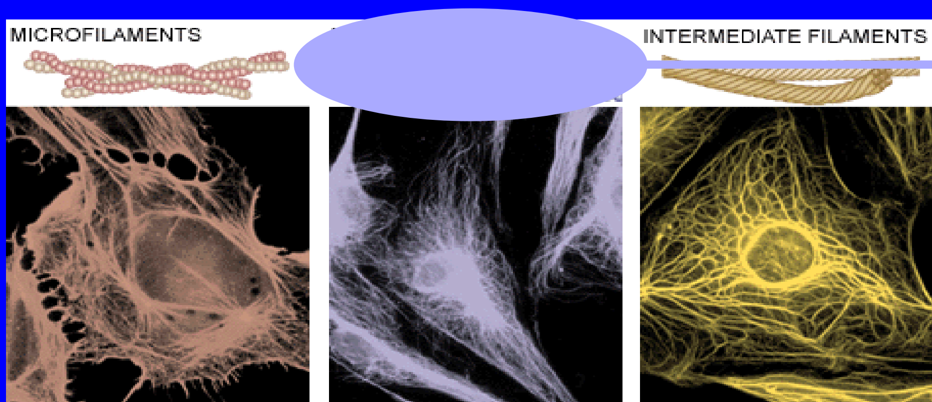


tiabendazol

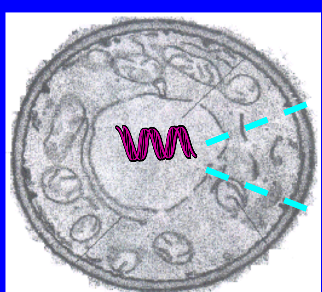


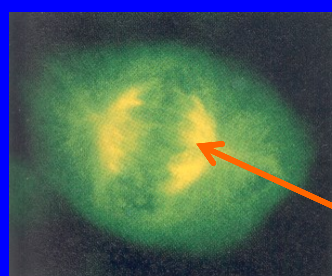
fuberidazole

Citoesqueleto em células eucarióticas



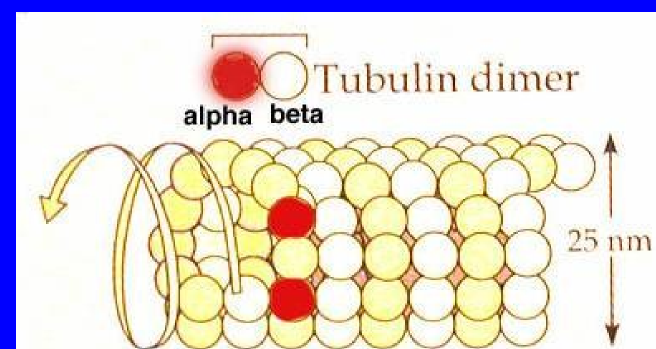
http://www.youtube.com/watch?v=PvDlIBgoSs





Divisão nuclear

Fuso mitótico



Benzimidazóis

Inibição da biossíntese de tubulina – proteína de microtúbulos do fuso mitótico

Efeito semelhante à colchicina (anti-câncer) em animais

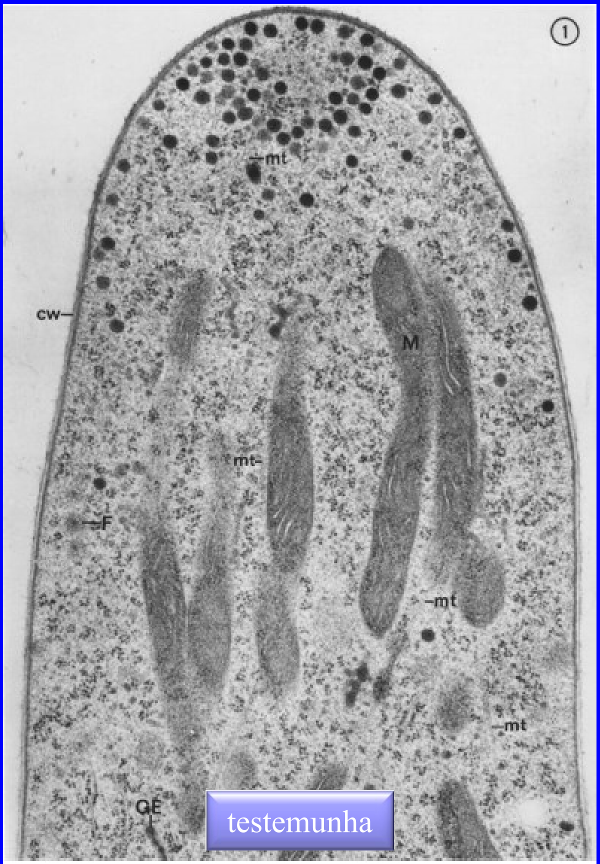
Bastante seletivos – afinidade às diferentes tubulinas determinam especificidade

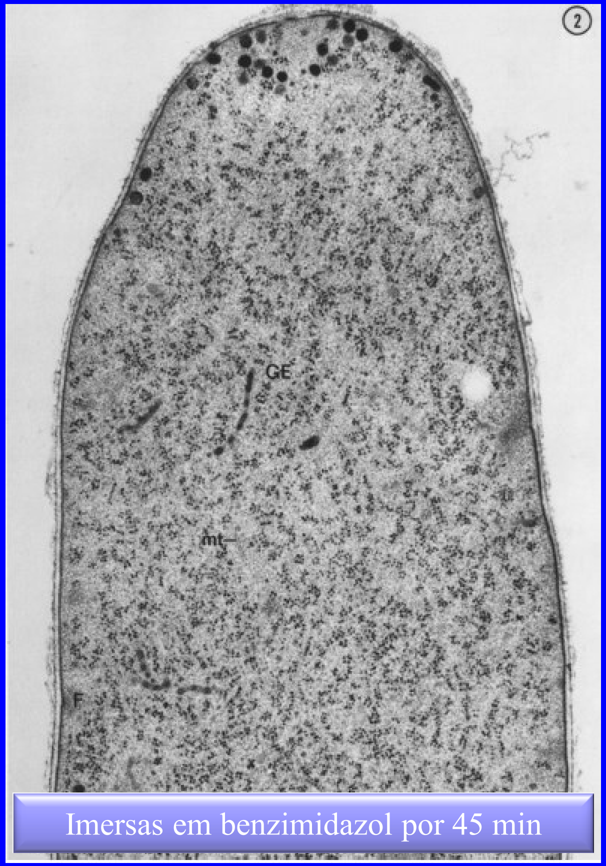
Cytoplasmic Microtubules and Fungal Morphogenesis: Ultrastructural Effects of Methyl Benzimidazole-2-ylcarbamate Determined by Freeze-substitution of Hyphal Tip Cells

RICHARD J. HOWARD and JAMES R. AIST
Department of Plant Pathology, Cornell University, Ithaca, New York 14853. Dr. Howard's present address is the Biochemicals Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, Delaware 19898.

Hyfas de *Fusarium acuminatum*

mt = microtúbulo
cw = parede celular
M = mitocôndrio
GE = aparato de Golgi





BENZIMIDAZÓIS

<u>CARACTERÍSTICAS</u>

- Atividade protetora (adesão à superfície e degradação lenta)

- Atividade curativa (translocação acropétala via apoplasto)
    - tiofanato-metílico
    - carbendazim
    - tiabendazol

Velocidade de translocação em maçãs

- Razoável espectro de ação antifúngica (menor em basidio)

- Baixa fitotoxicidade

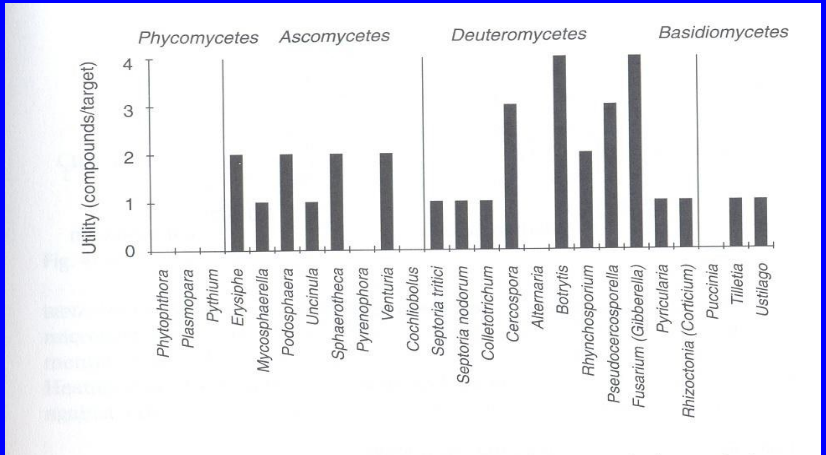


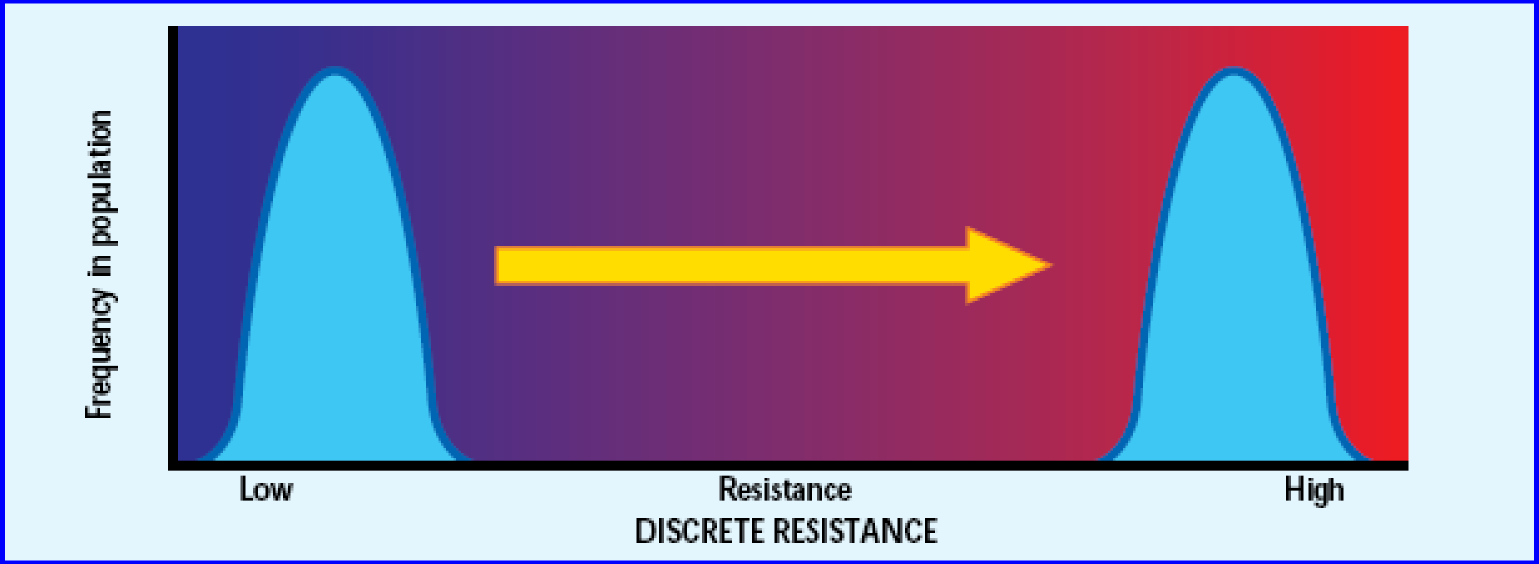
Fig. 4.31. Major use spectrum of a range of benzimidazole tubulin biosynthesis inhibitors.

Resistência de fungos a benzimidazóis

Resistência por redução de afinidade, monogênica

	Neurospora		*Saccharomyces*
fenilalanina →	tirosina	ou arginina →	histidina
$C_9H_{11}NO_2$	$C_9H_{11}NO_3$	$C_6H_{14}N_4O_2$	$C_6H_9N_3O_2$

Resistência durável

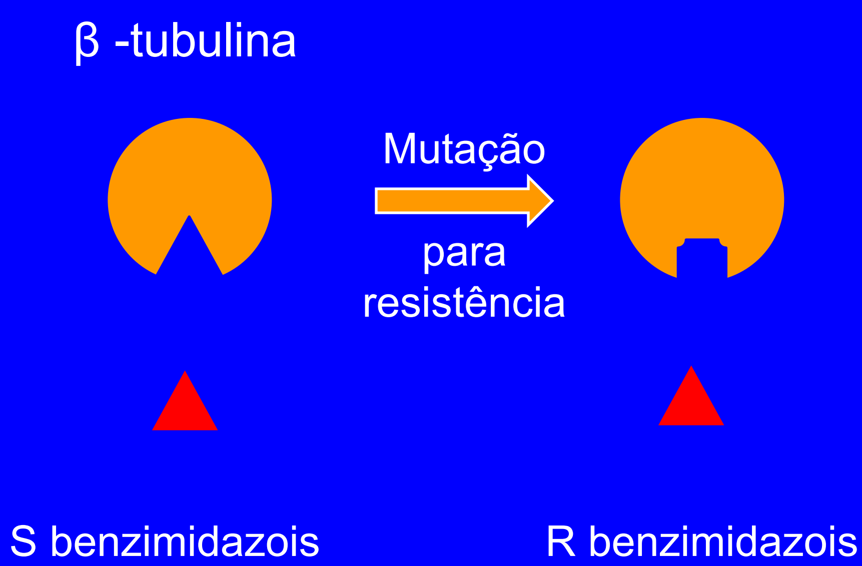


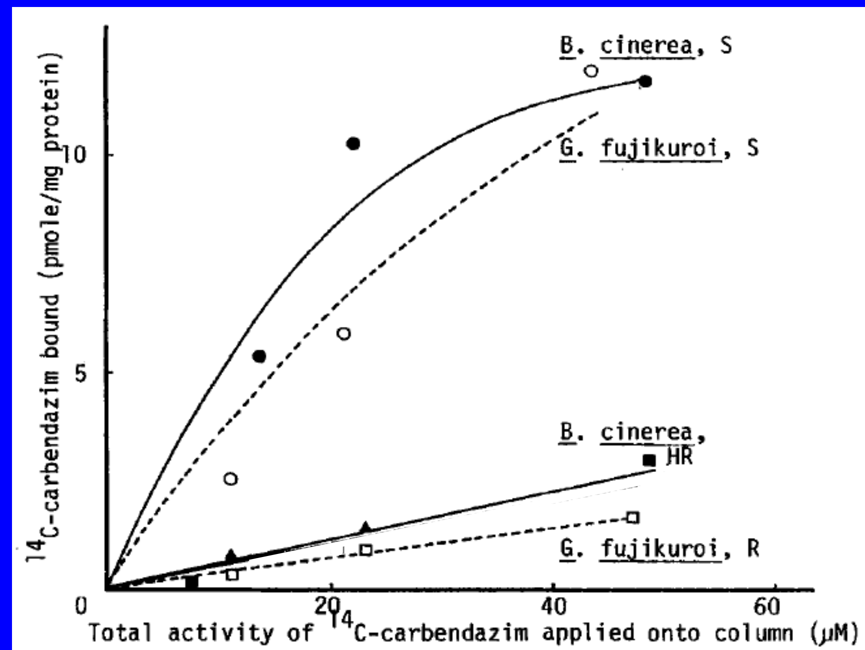
Resistência de fungos a benzimidazóis

Resistência por redução de afinidade, monogênica

Mutações no gene da $ß_1$-tubulina nas posições 50, 198, 200 e 240 – Resistência total

Ishii, H. (1992)





Binding of [14]Ccarbendazim in cell-free mycelial extracts of Botrytis cinerea and Gibberellafujikuroi isolates with different levels of resistance to carbendazim. (Levels of resistance to carbendazim: R, resistant to carbendazim; HR, highly resistant to carbendazim; S, sensitive to carbendazim).Ishii & Takeda(1988).

Literatura consultada

Davidse, L. C. Benzimidazole fungicides: mechanism of action and biological impact. Ann. Rev. Phytopathol. 24: 43-65. 1986.

Dorrance, A.E., Draper, M.A.; Hershman, D.E. Using foliar fungicides to manage soybean rust. The Ohio State University. 2007.

Delen, N. & Tosun, N. Fungicidas: mecanismo de ação e resistência. Parte I: Fungicidas com mecanismo de ação não-específica. RAPP 11:43-69. 2003.

Delp, C.J. Benzimidazole and related fungicides. In: Lyr, H. Modern Selective Fungicides.Gustav Fischer Verlag, New York. 1995. pp.291-303.

Epstein, L. Fifty years since silent spring. Annual Review of Phytopatology 52: 377-402, 2014.

Gullino, M.L. et al. Mancozeb: Past, present and future. Plant Dis. 94:1076-1087. 2010.

Hsu, F.G. et al. Study of root uptake and xylem translocation of cinmethylin and related compounds in detopped soybean roots using a pressure chamber technique. Plant Physiol. 93, 1573-1578. 1990.

Kimati, H. Controle químico. In: Manual de Fitopatologia, v.1, 4 ed. 2011

Montag et al. An *in vitro* study of the nature of protective activities of copper. J. Phytopathology 154:474-481. 2006.

Mueller, D.S., Wise, K.A., Dufault, N.S., Bradley, C.A., Chilvers, M.I. Fungicides for field crops. APS. 2013.

Oliver, R.P. & Hewitt, G. Fungicides in Crop Protection. 2nd. ed. CABI. 2014.

Rosskopf, E.N.; Chellemi, D.O.; Kokalis-Burelle, N.; Church, G.T. Alternatives to Methyl Bromide:
A Florida Perspective. APSNET Features, June 2005.

Sicbaldi, F. et al., Root uptake and xylem translocation of pesticides from different chemical classes. Pestic. Sci. 50, 111-119. 1997.

Williams, J.S. & Cooper, R.M. The oldest fungicide and newest phytoalexin – a reappraisal of the fungitoxicity of elemental sulphur. Plant Pathology 53, 263–279. 2004.
José Veiga (Syngenta) – imagens de absorção de fungicidas