

# Enhancing metalaxyl breakdown and its implications in Australian Horticulture

Hoong Pung Serve-Ag Research

Project Number: VX00012

### VX00012

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The research contained in this report was funded by Horticulture Australia Ltd with the financial support of the potato and vegetable industries.

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### ISBN 0 7341 0370 0

Published and distributed by: Horticultural Australia Ltd Level 1 50 Carrington Street Sydney NSW 2000

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# Enhanced metalaxyl breakdown and its implication in Australian horticulture

# Final Report

Horticulture Australia Project VX00012 (Project completion 30/12/01)

by

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Serve-Ag Research

January 15, 2002

# Horticulture Australia Project VX00012

Principal Investigator

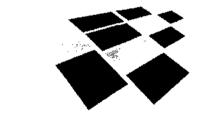
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This is a final report of project VX00012 - Enhanced metalaxyl breakdown and its implication in Australian horticulture.

The project was funded by Horticulture Australia Limited.





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# **Media Summary**

This one-year project funded by Horticulture Australia Limited was to review and compile information on the implications of enhanced metalaxyl breakdown, and to recommend management practices to minimise the risks associated with the fungicide's use in Australian horticulture.

Metalaxyl is highly effective against serious diseases, such as potato late blight, downy mildew and damping-off of vegetables or cavity spot on carrots. As a result, it is often the only fungicide used in horticulture to control soil borne diseases caused by *Phytophthora* and *Pythium*.

Unfortunately, metalaxyl is susceptible to enhanced degradation by soil microorganisms, if used repeatedly over a short period. In soils with an enhanced degradation problem, metalaxyl breaks down so rapidly that it does not provide appropriate disease control.

Excessive use of metalaxyl as a soil fungicide will lead to a reduction in disease control. For example, in a sandy soil that had no prior history of metalaxyl application, its half-life was longer than 10 weeks. This was reduced to as little as 4 days in paddocks with enhanced degradation. A single metalaxyl application may create a potential problem.

Biodegradation by soil microorganisms is the most important factor in reducing metalaxyl persistence in soils, however other factors play a role. These include chemical degradation, adsorption onto soil particles, leaching, run-off, and photo-decomposition. Metalaxyl degradation also varies with soil type, environmental and management conditions.

Growers and agricultural advisers must be aware of the consequences of excessive metalaxyl use. A better understanding of the fungicide's properties, as well as effects of soils, irrigation, and cultural practices, will help to maintain metalaxyl products availability for use against major, economically significant soil borne diseases.

An information leaflet on enhanced metalaxyl degradation and other factors that may influence its persistence and efficacy, and recommendations for its sustainable use, was prepared for growers and industry use.

# **Technical Summary**

This one-year project funded by Horticulture Australia Limited was to review and compile information on the implications of enhanced metalaxyl breakdown, and to recommend management practices to minimise the risks associated with the fungicide's use in Australian horticulture.

This report provides an overall perspective on enhanced degradation of metalaxyl, as well as other factors that affect metalaxyl persistence in agricultural systems.

Metalaxyl is highly effective against serious diseases caused by *Oomycetes* fungi, such as potato late blight, downy mildew and damping-off on vegetables, or cavity spot on carrots. As metalaxyl is a site-specific fungicide that is also very selective in its activity against target fungal pathogens, it is susceptible to both fungicide resistance and rapid degradation. The development and impact of metalaxyl resistance is well known. However, the phenomenon of rapid degradation of fungicides such as metalaxyl is relatively new, and there have been very few studies on its impact on *Oomycetes* disease control in horticultural crops.

It should be noted that although pesticide biodegradation in soil may adversely affect the control of soil pests, this process is also an important mechanism for degrading, detoxifying, or assimilating pesticides. This helps to prevent a build-up of pesticide residues, and soil and groundwater contamination.

# Enhanced biodegradation

- Enhanced biodegradation by soil microorganisms was found to be the most important factor in reducing metalaxyl persistence in soils.
- Enhanced biodegradation can be defined as the accelerated degradation of a pesticide after repeated applications to soils.
- Enhanced degradation of metalaxyl has been reported in sites that have a history of consecutive years of metalaxyl soil applications.
- In soils with an enhanced degradation problem, metalaxyl breaks down so rapidly that it
  does not provide appropriate disease control. For example, in a sandy soil that had no
  prior history of metalaxyl application, its half-life was 82 days. This was reduced to as
  little as 4 to 10 days in paddocks with enhanced degradation.
- In laboratory studies, a single exposure of different soils with no history of metalaxyl
  treatment was sufficient to increase their subsequent capacity to degrade the fungicide.
  This may be due to the wide range of microorganisms (fungi, bacteria and actinomycetes)
  capable of degrading it.
- In comparison to the soil system, most plant canopies do not support high microbial activities. Hence, enhanced degradation is unlikely to occur on plant canopies following metalaxyl spray applications.
- High microbial activity in soil is usually associated with high organic matter levels.
   Therefore, metalaxyl tends to degrade faster in soils that are high in organic matter.

# **Technical Summary (Cont.)**

- The rate of metalaxyl degradation in soils can also vary with soil depth. Organic matter levels are lower with increasing soil depth and hence conditions are believed to be less favourable for its degradation.
- Cultural practices may influence the persistence of metalaxyl in soil. Enhanced degradation was not detected in intermittently cropped red ferrosol soils in Tasmania. These soils had two or four years of pasture in between crops and metalaxyl soil applications.
- In contrast, rapid degradation was found in intensively cropped soils, where the fungicide
  had been applied to soil in carrot and potato crops in consecutive years.
- Further studies are required in order to better understand the effects of cropping practices, metalaxyl use, and types of crops, on metalaxyl persistence.
- It is not known whether affected soils can recover from enhanced metalaxyl degradation.
   Further investigations are required to determine the recovery potential of enhanced degradation affected sites.

# Other factors influencing persistence and efficacy

- Although, as a soil fungicide, metalaxyl is susceptible to biodegradation, there are additional factors that may influence its persistence and efficacy.
- Metalaxyl, with its high solubility, is easily transported in water. As a result, the mobility of
  metalaxyl is highest in sandy soils with low organic matter, and it may be leached down
  the soil profile with high rainfall or irrigation.
- Metalaxyl is less mobile in soils with high clay and/or organic matter due to higher adsorption onto soil particles. This makes less chemical available for degradation by soil microorganisms.
- Metalaxyl may also be susceptible to run-off, either mixed in with the run-off water or bound to eroding soil.
- The high solubility of metalaxyl offers one advantage; it is readily taken up by plants in solution. As a result, low dosages (~10ug/ml) often give effective control of Oomycetes fungi and good residual activity in soil. Phytophthora erythroseptica (pink rot) is sensitive at above 1ppm and completely inhibited at 10ppm metalaxyl, and the ED50 of Pythium sulcatum (cavity spot) is less than 5ug/ml metalaxyl.
- Metalaxyl degraded more rapidly at a pH of 8 or above. For example, less than 5% of the initial amount remained in solution after 12 weeks in sterile water at pH 10.
- Exposure to sunlight may also reduce the persistence of metalaxyl. Under simulated sunlight, the half-life of metalaxyl in soil was three to four times lower.
- The efficacy of metalaxyl for disease control is also influenced by the susceptibility of plant
  varieties and its effect on a fungal pathogen. Excellent disease control with metalaxyl can
  be obtained with the use of a *Phytophthora* resistant plant cultivar, while with a susceptible
  cultivar, disease symptoms can only be delayed as long as the fungicide persists in the
  soil.

# **Technical Summary (Cont.)**

- Metalaxyl tends to inhibit the pathogen, thereby preventing or reducing new infections, and reducing disease severity on infected plants, but it does not eradicate or kill the pathogen.
- This is contrary to the misconception by growers that metalaxyl soil application will also kill
  fungi, and thus reduce pathogen levels. Metalaxyl appears to act mainly by inhibiting
  Oomycetes fungal growth and sporulation.
- In northern Tasmania, where most fields have a close rotation of potato crops, an
  increase in the incidence of pink rot has been observed in spite of metalaxyl soil
  applications. This suggests that there may have been a build-up of the pathogen's level in
  soil following several potato crops or volunteer potatoes. Again, this highlights the
  importance of reducing pathogen levels through appropriate cultural practices rather than
  relying on a suppressive fungicide alone.

# Metalaxyl use

- Growers must become aware of the consequences of excessive use of modern pesticides for soilborne pest control. In recent years, there have been increasing numbers of reports of enhanced degradation of metalaxyl and other pesticides by soil microorganisms.
- The industry must take steps to promote better use of metalaxyl in order to ensure its long-term availability and effectiveness against the economically significant diseases.
- A long-term and sustainable approach for major diseases caused by Oomycetes
  pathogens must involve other measures, namely an integrated disease management
  program that includes appropriate cultural practices, improved soil management, and
  biological control methods.

# Technology Transfer

An information leaflet on enhanced metalaxyl degradation and other factors that may influence its persistence and efficacy, and recommendations for its sustainable use, was prepared for growers and industry use.

# Recommendations

- A long-term approach for a sustainable metalaxyl usage must involve the following measures for integrated disease management:
  - Use suitable crop rotations with plants that are not susceptible to Oomycetes fungal pathogens, thereby reducing the frequency of metalaxyl applications.
  - Do not plant one susceptible root crop soon after another.
  - Use crop cultivars with moderate to high resistance to Oomycetes pathogens.
  - Reduce metalaxyl leaching and run-off, by reducing the slope, avoiding over irrigating, constructing drainage ditches, and improving soil management to reduce compaction.
  - Encourage soil management practices that improve soil structure for better water infiltration, increased biological antagonists, disease suppression and reduced pathogen levels.
  - Develop alternative chemical methods for use in alternation or in addition to metalaxyl
    for *Oomycetes* soilborne disease control. For example, a new class of systemic
    fungicides that can activate plant natural defences may offer a new perspective in
    disease control.
  - Develop and introduce the use of biological control methods. As metalaxyl is selective
    in its activity, it is likely to be compatible with most biological control methods.
- Further studies are recommended in order to obtain a better understanding of the effects of cropping practices, types of crops, and intervals between metalaxyl applications on its persistence.
- Further investigations are required to determine the recovery potential of enhanced degradation affected sites.

# Introduction

# Background

Metalaxyl, a phenylamide fungicide, is currently used to control many major fungal diseases caused by *Oomycetes* fungi, such as *Pythium*, *Phytophthora*, and *Peronospora* (downy mildew) in vegetables, potatoes and field crops. Major diseases caused by *Oomycetes* fungi include cavity spot of carrots, and pink rot and late blight diseases of potatoes. In recent years, there have been increasing reports of enhanced metalaxyl breakdown by soil microorganisms. This process reduces the persistence of metalaxyl in soil, thereby affecting its efficacy for disease control.

Apart from microbial degradation, there are also other factors that may affect metalaxyl persistence in soils. Hence, this report will review and discuss all factors that are known to affect metalaxyl persistence and availability in soils.

As land use for agricultural production becomes more intensive, the use of metalaxyl is also expected to increase, as it has often been found to provide the most effective fungicide treatment for the control of diseases caused by *Oomycetes* fungi. Therefore, it is imperative that the horticultural industry has a good understanding of metalaxyl dissipation or loss in soil over time, and its implication for disease control. Unless the proper use of metalaxyl is promoted to the relevant industries, the long-term use of metalaxyl against the major target diseases may be severely affected.

## Aims

The aim of this project is to obtain an overall perspective of metalaxyl persistence in agricultural systems. As there is a lack of detailed information on metalaxyl degradation in horticultural crops in Australia, much of the information presented in this report is drawn from overseas studies, as well as environmental studies on pesticide leaching and groundwater contamination.

# **Metalaxyl Persistence**

# Persistence of pesticides - general\*

\* Reference of this section obtained from J. Jenkins & T. M. Smith

### Introduction

The fate and behavior of a pesticide in soil is governed by a variety of physical, chemical and biological processes, which are often complex and dynamic. Table 1 provides chemical properties for metalaxyl and some common pesticides. Most information on pesticide behaviour in soil is the result of research conducted to determine the impact of pesticides on groundwater contamination. Nevertheless, all the factors considered are also relevant to pesticide persistence, availability to crops, and hence disease control. In order to understand pesticide persistence in soil, we must first understand the different factors that are involved. Therefore, in this section, the important properties of pesticides in soil and their definition are introduced and discussed as a prelude to the section on metalaxyl persistence.

### Half-life

Pesticide persistence is usually expressed in terms of "half-life". This is the typical length of time needed for one-half of the total amount applied to break down to non-toxic substances. Local conditions such as climate and soil type have an important impact on the soil half-life of pesticides.

### Solubility

Water solubility is determined by the amount of a pesticide that will dissolve in a known amount of water, and is usually expressed in milligrams per litre (mg/L) or ppm of water.

The degree of pesticide uptake by plants is partially determined by the pesticide's water solubility; higher water solubility is related to a greater possibility for plant uptake.

### Adsorption

Adsorption is the binding of chemicals to soil particles. The degree of pesticide adsorption is determined by the chemical properties of the pesticide as well as soil texture (relative proportions of sand, silt and clay), moisture, and organic matter content. Soils high in organic matter or clay tend to be most adsorptive, and sandy soils low in organic matter least adsorptive. Therefore, the higher the organic matter content of the soil, the more adsorptive the soil; decreasing the likelihood that the pesticide will move from its point of application.

The degree of pesticide adsorption is often represented by the ratio of the amount of pesticide in the soil water to the amount adsorbed to the soil particles. This ratio is called the adsorption coefficient, or Kd. The Kd value for a pesticide is soil-specific and will vary with soil texture and organic matter content. Therefore, another pesticide coefficient, which is less soil-specific than the Kd, can be used in estimating pesticide persistence. This second coefficient, called Koc, is simply the Kd divided by the percent organic carbon in the soil. Organic carbon is a major component of soil organic matter.

The higher the Koc value, the greater the pesticide adsorption. Soil adsorption also influences the rate of pesticide degradation and plant uptake. Pesticides that are strongly adsorbed to soil particles are less available for microbial degradation and plant uptake.

### Mobility

Pesticides that are tightly bound to the soil may only move a few inches from the point of application, regardless of the amount of infiltrating water, whereas pesticides that are not bound as tightly may move many centimetres. Pesticides that are highly water soluble, relatively persistent, and not readily adsorbed by soil particles (low Koc) have the greatest potential for movement. Due to their lower adsorptive capacity and higher infiltration rates, shallow, sloping, sandy soils that are low in organic matter are the most vulnerable to pesticide leaching and groundwater contamination.

### Run-off

Run-off, the movement of chemicals in water over a sloping surface, can carry with it pesticides that are either mixed in with the run-off water or that are bound to eroding soil. The severity of pesticide run-off depends on several factors, many of which influence the rate of water infiltration into the soil. These include the grade or slope of an area; the texture and moisture content of the soil; the amount and timing of irrigation or rainfall; and the presence of vegetation or plant residues.

### Microbial degradation

Microbial degradation is the breakdown of chemicals by microbial organisms. It occurs when fungi, bacteria, and other microorganisms in the soil use pesticides as food or other energy source, or consume the pesticides along with other sources of food or energy. Soil organic matter content, moisture, temperature, aeration, and pH all affect microbial degradation. Microbial activity is usually high in warm, moist soils with neutral pH.

### Chemical degradation

Chemical degradation of pesticides can occur when the pesticides react with water, oxygen, or other chemicals in the soil. Chemical degradation usually increases as soil pH becomes extremely acidic or alkaline.

Sunlight may also breakdown pesticides (photodegradation). Factors affecting pesticide photodegradation include the intensity of the sunlight, length of exposure, the application site and/or method, and the chemical properties of the pesticide.

### Volatilization and plant uptake

Apart from degradation, pesticides may move from the point of application via volatilization, leaching, and plant uptake. Volatilization is the loss of pesticide as it changes from a liquid or solid to a gas, and vaporizes from the soil or plant surface into the atmosphere. The rate of volatilization is determined by the vapor pressure of the pesticide (which is a function of the chemical properties of the pesticide and temperature) and the extent to which the pesticide is adsorbed (or held) on plant and soil surfaces. Higher temperatures usually result in increased volatilization.

# Chemical properties of metalaxyl

The chemical name for metalaxyl is N-(2,6-dimethylphenyl)-N-(methoxyacetyl)-alanine methyl ester (Fig. 1a, Droby & Coffrey 1991).

Compared to many other pesticides, metalaxyl has a low adsorption coefficient (Koc) and high solubility (Table 1). As a result of these properties, it would not bind readily to soil particles, and is easily transported in water (Bailey & Coffrey 1984, Cohen & Coffrey 1986, Sharom & Edgington 1982).

Fig. 1. Metalaxyl (a) and its acid metabolite (b).

### Mode of action

The biochemical mode of action of metalaxyl on *Phytophthora* and *Pythium* involves the inhibition of RNA synthesis (Cohen & Coffrey 1986).

Metalaxyl is transported predominantly in an acropetal direction through roots, stems, and leaves in the transpiration channel (Gupta et al. 1985, Staub et al. 1978, Zaki et al. 1981). Metalaxyl acid (Fig. 1b, Droby & Coffrey 1991), produced by hydrolysis of the ester group, is much more phloem mobile. It is the main breakdown by-product of metalaxyl in soils (Droby & Coffrey 1991, Edgington 1981). Unfortunately, metalaxyl acid possesses no fungistatic properties (Edgington 1981).

Metalaxyl acts mainly by inhibiting *Oomycetes* fungal growth and sporulation. It prevents sporangial formation of *Oomycetes* fungi (Malajczuk et al. 1983). Metalaxyl does not eradicate the fungi in soil but rather acts as a fungistat and suppresses their activity (Hamm et al. 1984, Coffrey & Young 1984, Hickey & Coffrey 1980).

In soils, low dosages (~10ug/ml) often give effective control of *Oomycetes* fungi (Kannwisher & Mitchell 1978). The high sensitivity of the sporangia production of some *Oomycetes* fungi to metalaxyl, may have contributed to the good residual activity of metalaxyl in soils (Cohen & Coffrey 1986). *Phytophthora erythroseptica* (pink rot) is sensitive at above 1ppm and completely inhibited at 10ppm metalaxyl (Oxspring et al 2000), and the ED50 of *Pythium sulcatum* (cavity spot) was less than 5ug/ml metalaxyl (Davison & McKay 1999).

There is also evidence of an interaction between antagonistic microorganisms and metalaxyl. A low concentration of metalaxyl (10 mg/litre) resulted in almost complete hyphal cell death (lysis) of *Phytophthora* in non-sterile soil solution compared to approximately 50% lysis in sterile soil solution (Malajczuk et al. 1983). It is possible that the suppression of *Oomycetes* fungi by metalaxyl in soil increased the activities of lytic microorganisms (Malajczuk et al. 1983). This may account for the enhancement of disease suppression of *Phytophthora* with metalaxyl application in suppressive soils without affecting its biological antagonists (Allen et al. 1980).

Table 1: Chemical properties for metalaxyl and some common pesticides

The pesticides are grouped according to small, medium or large teaching potential, taking into consideration the half-life, solubility and Koc values.

Chemical properties of pesticides commonly used on greenhouse crops (from SCS/ARS/CES Pesticide Properties Database).					
Pesticide common	Trade name	½ life (days)	Solubility (ppm)	Koc	
name				<u> </u>	
		II Leaching Potent	ial		
Insecticides and Miti	icides	<b></b>			
ACEPHATE	Orthene, PT1300	3	818000	2	
DICOFOL	Kelthane	60*	1*	180000*	
ENDOSULFAN	Thiodan	50	0.32	12400	
FLUVALINATE	Mavrik	30*	0.005	1000000*	
MALATHION	Malathion	1	130	1800	
METALDEHYDE	Bug-Getta, Slugit	10*	230	240	
NALED	Dibrom	1	2000	180	
OXAMYL	Oxamyl, Vydate	1	2000	25	
PERMETHRIN	Pramex, Pounce	30	0.006	100000	
PROPARGITE	Ornamite	56	0.5	4000*	
Fungicides					
CHLOROTHALONIL	Daconil	30	0.6	1380	
MANCOZEB	Dithane M-45	70	6	2000	
PCNB	Terraclor 75 WP	21	0.44	5000*	
	Larg	ge Leaching Potent	tial		
Fungicides			· · · · · · · · · · · · · · · · · · ·		
BENOMYL	Beniate, 50 DF	240	2.0	1900	
METALAXYL	Subdue 2 E, 2 G	70	8400	50	
TRIFORINE	Triforene, 18.2EC	27	30	540*	

<sup>\*</sup>Estimated values are used where there is insufficient data. Table from J. Jenkins, & T. M. Smith

# Enhanced metalaxyl degradation

### Occurrences

There have been many reports of enhanced degradation of metalaxyl in soils that have a history of metalaxyl soil applications (Davison & McKay 1999, Papini & Andrea 2001, Sharom & Edgington 1982 & 1986, Bailey & Coffrey 1984, Droby & Coffrey 1991). In Australia, enhanced degradation was found in intensively cropped carrot soils that have a history of consecutive metalaxyl applications (Davison & McKay 1999, 2001).

In soils with no previous history of applications, metalaxyl may persist for several months, whereas similar soils that have prior history of metalaxyl treatment were reported to have enhanced degradation (Sharom & Edgington 1982, Bailey & Coffrey 1984). For example, in two different soils with the same history, the half-life of metalaxyl was 14 and 28 days respectively, compared to the equivalent non-treated soils, which had half-life in excess of 10 weeks (Bailey & Coffrey 1984). A half-life of only 6 days was recorded in a sandy soil that had six previous metalaxyl treatments (Droby & Coffrey 1991).

## Microbial biodegradation

Biodegradation or degradation by soil microorganisms appeared to be the most important cause of reduced metalaxyl persistence in soil. However, there appeared to be no specific microorganisms linked to the biodegradation process. Both bacteria and fungi have been associated with the degradation of metalaxyl. Metalaxyl was rapidly degraded by various microflora isolated from sandy loam soils, with and without a history of metalaxyl applications (Bailey & Coffrey 1984). In chloroform-sterilised soil, however, little or no degradation occurred.

Fungi and bacteria that could actively degrade metalaxyl were isolated equally from control (no history of metalaxyl) and problem soils (Bailey & Coffrey 1985). Isolated fungi included Acremonium recifei, Aspergillus flavus, Caldosporium herbarum, Fusarium solani, Penicillium variabile, and Trichorderma hamatum (Bailey & Coffrey 1986). The isolated bacteria were Bacillus cereus, Corynebactrium sp., Pseudomonas acidovorans, P. delafieldii and Streptomyces albolongus (Bailey & Coffrey 1986). In soils, these organisms metabolise metalaxyl to nonfungistatic acylanilides, principally metalaxyl acid.

The addition of the fungicide thiram or the antibiotics streptomycin and chloroamphenicol to an avocado soil resulted in 75% and 51% inhibition of the metalaxyl degradation, respectively (Droby & Coffrey 1991). A combination of the fungicide and antibiotics resulted in 89% inhibition. The almost complete inhibition of metalaxyl degradation by the combined thiram and antibiotics indicates that a wide range of microorganisms (fungi, bacteria and actinomycetes) is responsible for its breakdown in soils. The predominant microorganisms isolated from the soils were *Fusarium* sp., *Trichoderma* sp., *Penicillium* sp., *Bacillus* sp. and various actinomycetes (Droby & Coffrey 1991).

### Metabolic process

The metabolism process of metalaxyl appeared to be one of cometabolism, as no organisms were found that could use metalaxyl as a sole carbon source (Bailey & Coffrey 1985, 1986).

In contrast to mineralization, no net energy is derived during cometabolism (Alexander 1981). Metalaxyl appeared to be mainly transformed to metalaxyl acid. The metabolic pathway of metalaxyl transformation is not known. However, many pesticides are incidentally transformed in soil by microbial enzymes (Felshot & Shelton 1993). This may explain the lack of evidence in linking specific groups or types of microorganisms to enhanced biodegradation in some studies (Droby & Coffrey 1991).

Mineralization of metalaxyl was not a principal cause of metalaxyl dissipation in soil (Sukul & Spiteller 2001a). Some studies on metalaxyl degradation were based on detecting mineralized by-products of metalaxyl, such as radioactive carbon dioxide (Sigler et al 1997, Papina & Andrea 2001). Although metalaxyl acid may be further broken down to simple by-products like carbon dioxide, the use of carbon dioxide measurements alone may not be indicative of the rate of metalaxyl degradation.

### **Development of enhanced degradation**

In laboratory studies, a single exposure of different soils with no history of metalaxyl treatment was sufficient to increase their subsequent capacity to degrade the fungicide (Fig. 3, Droby & Coffrey 1991). This rapid enhancement of metalaxyl degradation may be due to the broad spectrum of bacteria and fungi that are capable of degrading it in soils.

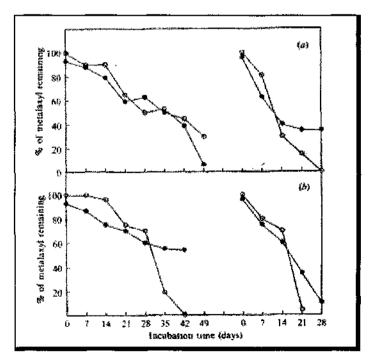


Fig 3. Degradation of metalaxyl in tobacco (a) and corn (b) soils, with no history of metalaxyl treatment (left) and after one application (right) (Droby & Coffrey 1991).

### Influence of metalaxyl concentration

The rate of metalaxyl degradation increased with increasing concentrations of the fungicide in soil (Fig. 4, Droby & Coffrey 1991). With increased concentrations of metalaxyl, the rate of the fungicide biodegradation was also faster in soil with a history of metalaxyl treatment, compared to one with no previous fungicide application.

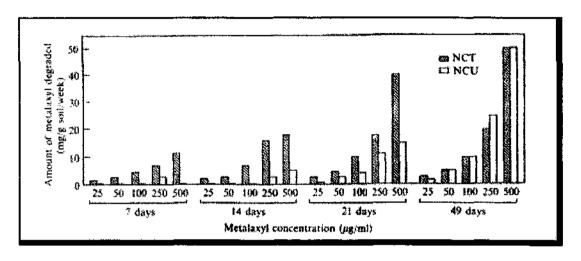


Fig 4. Influence of metalaxyl concentration on rate of biodegradation by tobacco soils with (NCT) and without (NCU) history of metalaxyl treatment (Droby & Coffrey 1991).

### Foliar vs soil application

While there has been evidence of enhanced degradation following metalaxyl application in soil systems, there have been little or no studies on metalaxyl degradation following foliar applications and seed treatments. There have been very few studies on the effects of multiple foliar applications on enhanced degradation on foliage or in soil.

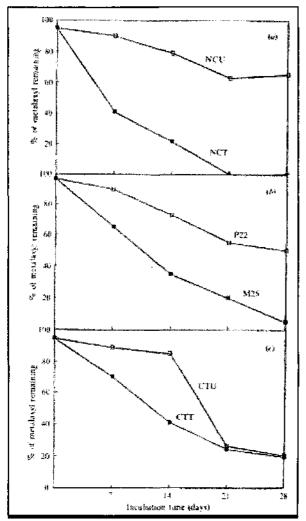
Field studies conducted in West Australia showed that foliar applications of metalaxyl reduced cavity spot due to *Pythium* infections on carrot roots sown in soil that had no prior history of metalaxyl use (Davison & McKay 1999). However, in soils with enhanced degradation problems, the foliar applications did not reduce cavity spot on roots.

In comparison to the soil system, most plant canopies do not support high microbial activities. There may be an exception with plants that have a dense leaf canopy, eg. turf-grass, which intercepts over 95% of applied pesticides and can also support a large microbial population (Sigler et al 1997). The dissipation rate of metalaxyl in a turf-grass system was rapid, with a half-life of 4 days after treatment (Sigler et al 1997), compared to 13.5 days on grapevines (Navarro et al. 2001).

### Soil properties

Enhanced biodegradation of metalaxyl was demonstrated in a range of soils differing in their physical properties and history of treatments. Different soil types with previous exposure to metalaxyl collected from different locations degraded the fungicide faster than similar soils with no history of exposure (Droby & Coffrey, 1991).

The rates of the degradation appeared to be influenced by soil properties, particularly with organic matter (Fig. 5, Droby & Coffrey 1991). In this case, the higher the organic matter, the faster the degradation rate. High organic matter usually increased microbial activities in soil. In some cases, high organic matter may slow degradation rate, as a result of increased adsorption of the fungicide (Fig. 7, Sharom & Edgington 1982).



NCU-tobacco soil, no metalaxyl; 4.3% clay, 16.6% silt, 79.1% sand, 0.9% organic matter, pH 5.5

NCT-tobacco soil, with metalaxyl; 5.3% clay, 16.5% silt, 78.2% sand, 0.9% organic matter, pH 5.7

P22-avocado soil, no metalaxyl, 8.1% clay, 17.0% silt, 74.9% sand, 4.9% organic matter, pH 7.5

M25-avocado, with metalaxyl, 7.0% clay, 14.1% silt, 78.9% sand, 4.5% organic matter, pH 7.5

CTU-tobacco soil, no metalaxyl, 23.1% clay, 30.2% silt, 55.7% sand, 6.8% organic matter, pH 7.0

CTT-tobacco soil, with metalaxyl, 21.4% clay, 33.5% silt, 51.8% sand, 4.9% organic matter, pH 6.5.

Fig. 5. Degradation of metalaxyl in tobacco (a), avocado (b) and citrus (c) soils at various incubation periods (Droby & Coffrey, 1991).

The rate of metalaxyl degradation in soils can also vary according to soil depth. In Western Australian sandy soil, the surface soil (0-25cm) has a half-life of 48 days compared to 117 days in the sub-surface (25-50cm) (Di et al 1998). Soil conditions are believed to become less favourable for pesticide degradation with increasing soil depth. The different soil layers contain different organic matter levels and microbial populations. The organic matter of subsurface soil (0.15% organic carbon, 15 ug microbial carbon/g soil) was lower than that of the surface soil (0.53% organic carbon, 21 ug microbial carbon/g soil) (Di et al 1998).

### **Cultural practices**

Previously, there has been no comparative study to determine the effects of metalaxyl applications and cropping practices. Fortunately, in the years 1999 and 2000, laboratory tests of ferrosol soils, a common soil type in the north-west coast of Tasmania, enabled such a comparison to be made (Table 2, Fig. 6). All the soil tests were carried out by Chemistry Centre WA, in Western Australia. Soils were sampled from carrot crops as part of project VG98011, and soils from a potato crop and a pasture from the Smithton area, were sampled by Mr Trevor Stebbings of Syngenta Crop Protection Pty Limited.

Table 2: The effects of metalaxyl applications, crop rotation and cropping practices on metalaxyl half-life in Tasmania

Paddock No.	Location	Soil type	Date soil sampled	Metalaxyl product applications	Crop	Cropping practice	Half-life in crop soil	Half-life in headland soil*
1	Don	Ferrosol	18-Nov-99	Skg/ha Ridomil MZ with 3 foliar sprays on poppies; 20kg/ha Ridomil 25G on potatoes and 3 sprays of Ridomil MZ for late blight control.	poppy 99, potato 98/97, carrot 96	intensive	13	5.7
2	Kindred	Ferrosol	12-Nov-99	Bidomil 350 poil postication	carrot 99, ryegrass 99, potato 99/98	intensive	9.1	11.4
3	Kindred	Ferrosol	12-Nov-99	Ridomil 25G soil application - 40kg/ha on carrots at seeding; 20kg/ha on potatoes.	pyrethrum 99, carrot 99/98, grass 98, potato 98/97	intensive	11.1	12
4	Kindred	Ferrosol	8-Apr-99		carrot 99, tema grass 99, potato 98/97	intensive	13.5	21.1
5	Kindred	Ferrosol	12-Nov-99	Ridomil 25G soil application - 20kg/ha on carrots and potatoes	carrot 99, pyrethrum 99-95, potato 95	Intermediate (but previously intensive)	13.2	23.9
6	Sheffield	Ferrosol	15-Nov-99	Ridomil 25G soil application - 20kg/ha on carrots at seeding, 22kg/ha on potatoes.	carrot 99, fallow/grass 98-97, potato 96	intermediate	>30; ND**	>30; ND
7	Smithton	Ferrosol	15-May-00	Ridomil 25G soil application - 20kg/ha on potatoes and 2 sprays of Ridomil MZ for pink rot control; pea seeds treated with Apron.	potato 00/99, last potato 95/96; grass & 3 months pea crop in between	intermediate	>40; ND	NT***
8	Smithton	Ferrosol	15-May-00	Nil	grass only	pasture only	40	NT

<sup>\*</sup> Headland soils - soil samples taken from row close to fence line, where no carrots were sown and soil was untreated.

Paddocks 7 and 8 are adjacent to one another – soil from Paddock 7 taken from top of sloping ground where pink rot incidence was 80% or more. Pink rot incidence was relatively low on level ground with less than 10% potatoes affected.

<sup>\*\*</sup> ND = half-life not detected; \*\*\* NT = not tested

Enhanced metalaxyl degradation was found on soils collected from intensively cropped ground, where metalaxyl had been applied to soils every growing season in Paddocks 2, 3 and 4. These paddocks belong to the same grower and were managed in the same manner.

On carrots, Ridomil® 25G granules were applied into the soil at sowing for *Pythium* disease control. On potatoes, Ridomil® 25G granules were applied at planting and may have been followed by Ridomil® MZ foliar sprays for pink rot control, and a Ridomil® MZ foliar spray applied for late blight control. Apron® SD350 was applied onto pea seeds.

The metalaxyl rates used were 52.5g/100kg seed for peas, 1.6kg/ha in foliar sprays for late blight and 500g/ha in soil applications for pink rot control on potatoes, and 1kg/ha for *Pythium* and *Phytophthora* disease control on carrots.

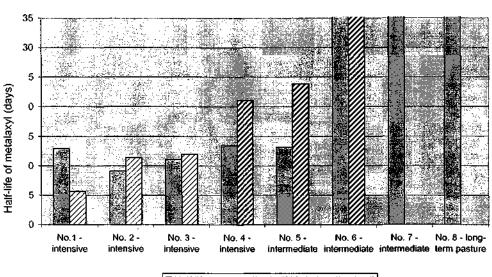


Fig. 6. The influence of cropping practices on the persistence of metalaxyl in soil

■Half-life in crop soil ☑ Half-life in headland soil

It appears that different cultural practices may influence the persistence of metalaxyl in soils (Table 2, Fig. 6). Of the three sites with intermittent or intermediate cropping practices, enhanced degradation was not detected in soils that had two and four years of pasture in between crops and metalaxyl soil applications (Paddocks 6 & 7). In contrast, rapid degradation was found in soil that had four years of pyrethrum in between carrot crops and metalaxyl applications (Paddock 5). There was no soil cultivation during the perennial pyrethrum crop, and metalaxyl was not used. However, with Paddock 5, prior to pyrethrum, the ground had been intensively cutivated and cropped over many years and had poor soil structure. Paddock 1 had been intensively cropped, but was considered to have intermittent metalaxyl soil application, where it was applied to soil only for pink rot control on potatoes. This suggests that soil structure and soil health, as influenced by management practices could also impact on the degradation rate, and that soil recovery from intensive cropping could take a long time.

The metalaxyl half-life in untreated headland soils from near fence lines, although usually higher than in the intensively cropped soil, tends to mirror the degradation rates found in the cropped soils. The width of the headland area in the paddocks can vary from year to year, and sometimes crops were sown very close to the fence line. As a result, there may be cross-contamination between treated and untreated soils.

### Recovery from enhanced degradation

There have been no studies conducted on whether affected soils can recover from enhanced metalaxyl degradation. Research on the rapid degradation of metham sodium showed that affected soils appeared to recover over time (Warton 2001, Warton et al. 2001).

As the microbial degradation of metalaxyl appeared to be cometabolism rather than mineralization, it is possible that the enhanced degradation may be reversible. Under the cometabolism process, the microbial population transforming it does not usually expand, and biodegradation would seem rapid only as long as favourable conditions exist (Felsot & Shelton 1993). However, further studies are needed to examine the reversibility of soils that have had consecutive years of metalaxyl applications.

### Testing for enhanced degradation

Most information on metalaxyl degradation in soils is based on research conducted under controlled laboratory conditions. This is because it is easier to determine pesticide degradation rates in laboratory tests. Under field conditions, there are many factors, eg. moisture, temperature, and composition of microbes, that can influence the degradation rate.

Laboratory measured degradation rates can be different from those measured under field conditions. The half-life of metalaxyl measured under controlled laboratory conditions (48 days) was lower than that measured under field conditions (70 days) (Di et al 1998). According to Di et al (1998), the longer field half-life of metalaxyl may be attributed to it leaching to below the surface layer, where the degradation of the fungicide was slower. It is also possible that the handling of soil samples used in laboratory incubation tests may have altered the composition and activity of microorganisms (Di et al 1998). This shows that metalaxyl half-life obtained under laboratory conditions are an indication of soil potential for enhanced biodegradation, and that the number of days determined would be subject to variations under field conditions.

In Australia, the Chemistry Centre WA in Western Australia has recently carried out laboratory tests to determine soil potential for enhanced degradation. The laboratory test for a soil sample takes about 5 weeks. The cost will vary depending on the number of soil samples being processed.

A sensitive bioassay method was developed for quantifying low concentrations of metalaxyl in soils (Bailey & Coffrey 1984). This bioassay was based on the highly significant linear correlation of the radial growth of an isolate of *Phytophthora boehmeriae* and the log concentration of metalaxyl. With this method, aqueous extracts of metalaxyl-treated soils were incorporated into commeal agar, and measurements were taken of the radial growth of the fungus following incubation of 5mm disks of the fungus on the resulting agar medium. The bioassay with *P. boehmeriae* detected metalaxyl concentrations ranging from 2 to 30 ng/ml.

Further studies would be required in order to develop a similar bioassay method with a local and metalaxyl sensitive isolate of *Pythium* or *Phytophthora*, for use in Australia.

# Other factors influencing metalaxyl persistence and efficacy

There are also other factors that may influence metalaxyl persistence and efficacy. A good understanding of these other factors is essential in the management of metalaxyl usage.

### **Mobility & Adsorption**

Compared to many other pesticides, metalaxyl has a high solubility and a low adsorption coefficient (Table 1). As a result of these properties, it is relatively mobile. The mobility of metalaxyl is highest in sandy soils with low organic matter (Sharom & Edgington 1982, Sharma & Awasthi, 1997). For example, following 10cm of simulated rainfall, muck soil that had very high organic matter had retained almost all of the metalaxyl on the surface of a soil column, while the fungicide had leached to the base of the soil column in a sandy loam soil (20cm depth) (Fig. 7, Sharom & Edgington 1982).

Higher fungicide adsorption onto soil also made less chemical available for degradation by soil microorganisms. Metalaxyl persisted longer (half-life of 9.5 weeks) in the muck soil compared to loam soil (half-life of 3.5 weeks). This study showed that organic matter can increase or decrease metalaxyl degradation, depending on its adsorption capacity and its microbial activities.

In India, Sukul Spiteller (2001b) found that metalaxyl half-life ranged from 36 to 73 days in non-sterile soil, depending on soil properties. A loss of 5.3% to 14.7% was found to be due to abiotic factors, particularly adsorption onto soils.

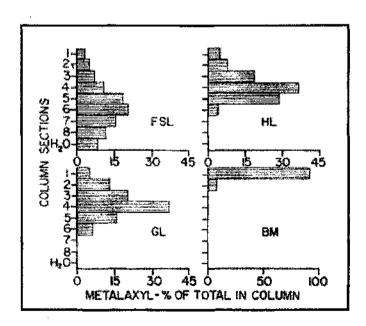


Fig. 7. Mobility of metalaxyl in four soils as affected by 10cm of simulated rainfall. Each column section was 2.5cm in depth. FSL (Fox sandy loam - 1.7% organic matter); HL (Honeywood loam - 4.5% organic matter); GL (Guelph loam - 5.7% organic matter; BM (Bradford muck - 62.8% organic matter).

Following 20cm of simulated rainfall, 87% of the metalaxyl was leached from a 20cm column of a soil containing 85% sand, 7.5% silt, 7.5% clay and 2% organic matter (Fig 8, Sharom & Edgington 1986). This indicates that with high rainfall or irrigation, metalaxyl may be leached down the soil profile.

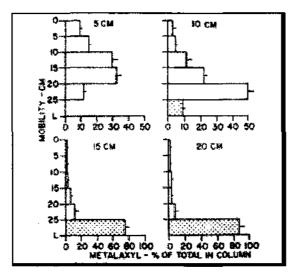


Fig. 8. Mobility of metalaxyl in soil column as influenced by 5, 10, 15 and 20cm of simulated rainfall (horizontal lines indicate standard deviation) (Sharom & Edgington 1986).

Under field conditions, the fungicide moved downwards when wet, and upwards as the soil profile became dry (Sharom & Edgington 1986). This phenomenon was known as the "yoyo' effect. Therefore, in spite of its high mobility, metalaxyl applied into soil tends to remain within reach of root systems.

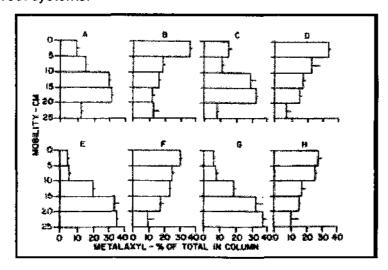


Fig 9. Movement of metalaxyl in soil columns as influenced by alternating periods of simulated rainfall and 48-hour dry spells (horizontal lines indicate standard deviations). (A) 5cm rain; (B) 5cm rain, one dry spell; (C) two 5-cm rains, one dry spell; (D) two 5-cm rains, two dry spells; (E) three 5-cm rains, two dry spells; (F) three 5-cm rains, three dry spells; (G) four 5-cm rains, three dry spells; (H) four 5-cm rains, four dry spells (Sharom & Edgington 1986).

There is still a potential of reducing metalaxyl concentrations through the leaching process, thereby reducing its efficacy in controlling diseases. This reduction in efficacy was demonstrated in a study (Sharom & Edgington, 1982), which showed that the fungicide gave effective control of white rust on radish seedlings grown in pots (soil depth of 15cm) when applied at 0.2kg/ha and not subjected to leaching (Table 3). However, disease severity increased when the treated soils were subjected to 10 and 20cm of simulated rainfall. The amount of fungicide lost is likely to be influenced by the soil adsorption capacity, and the amount and intensity of rainfall and irrigation.

Table 3: Effect of simulated rainfall on the efficacy of metalaxyl in controlling white rust of

radish (Sharom & Edgington 1982)

Simulated	Treatment (Metalaxyl kg/ha)	Disease index*		
rainfall (cm)		7 days after inoculation	14 days after inoculation	
0	0.0	8.0 a	10.0 <u>a</u>	
0	0.2	0.0 d	2.0 b	
10	0.2	2.0 с	8.0 a	
20	0.2	5.0 b	9.7 a	

<sup>\*</sup>Based on ratings of 0 to 10, with 0 = no infection, 10 = 100% affected. Within each column, values followed by the same letters are not significantly different at 5% level.

Run-off, the movement of chemicals in water over a sloping surface, can carry with it pesticides that are either mixed in with the run-off water or that are bound to eroding soil. The severity of pesticide run-off depends on several factors, many of which influence the rate of water infiltration into the soil. These include the grade or slope of an area, the texture and moisture content of the soil, the amount and timing of irrigation or rainfall, and the presence of vegetation or plant residues.

In northern Tasmania, many fields where horticultural crops are produced tend to have undulating ground. Soils in sloping ground usually tend to have higher sand content and lower clay and organic matter compared to low lying ground in the same paddock.

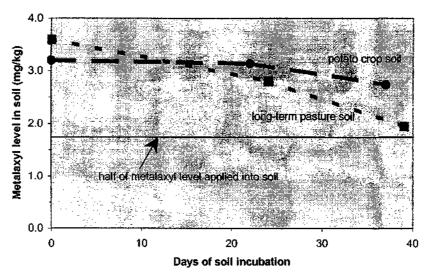


Fig. 10. Degradation of metalaxyl in treated potato soil and adjacent untreated pasture soil from Smithton, Tasmania, in a laboratory test.

The soils from Smithton (Table 2) were tested for enhanced biodegradation as a result of severe pink rot disease on tubers produced at the top of sloping ground in a potato crop. Soil was collected from the slope where pink rot was evident, and untreated soil from an adjacent field of long-term pasture was used for comparison. No enhanced biodegradation of metalaxyl was detected in the two soils (Table 2, Fig. 10). It is possible that the lack of disease control, may be due to fungicide run-off from the sloping ground.

Poor pink rot control also frequently occurred on potato tubers sown in compacted ground that has poor water infiltration, as well as on tubers near the top of potato moulds. These observations may be explained by loss of metalaxyl due to leaching and/or run-off.

### Chemical degradation

Chemical degradation of metalaxyl may occur with increasing pH. Metalaxyl was found to be persistent in sterile water of pH 3, 5, and 7, with more than 84% of the initial amount remaining in solution after 12 weeks (Sharom & Edgington 1982). Degradation of metalaxyl in water with pH of 8.1 was more rapid than in water of pH 3 to 7, and most rapid in pH 10, with less than 5% of the initial amount remaining in solution after 12 weeks.

Exposure to sunlight may also reduce the persistence of metalaxyl. Under simulated sunlight, the half-life of metalaxyl was three to four times lower in soil (Sukul & Spiteller 2001b).

### Effects on pathogen & plant susceptibility

The efficacy of metalaxyl for disease control is also influenced by the susceptibility of plant varieties and its effect on a fungal pathogen. Kannwischer & Mitchell (1978) showed that excellent protection from *Phytophthora parasitica var. nicotianae* was obtained on a resistant tobacco cultivar planted in metalaxyl treated soil. However, on a susceptible tobacco cultivar, infection and plant mortality by the pathogen was only delayed until approximately 50 days after planting, followed by a rapid increase in mortality, in metalaxyl treated soil (Kannwischer & Mitchell 1978). The rapid increase in plant mortality with the susceptible cultivar, which is likely to be due to degradation of metalaxyl, also coincides with an increase in the pathogen's inoculum level in soil. It appears that metalaxyl inhibits the pathogen, thereby preventing or reducing new infections and reducing disease severity on infected plants, but does not eradicate or kill the pathogen in infected plants and soils (Kannwisher & Mitchell 1978, Hamm et al 1984).

### Fungicide resistance

Effectiveness of a fungicide could be reduced with the development of resistant isolates of fungal pathogens. The risk of fungicide resistance was considered to be much lower with soilborne *Oomycetes*, since spore populations are presumed to be much lower, and soil places considerable constraints on their dissemination (Schwinn 1983). Problems could arise, however, with *Oomycetes* pathogens such as *Peronospora* spp. (downy mildew) and *Phytophthora infestans* (late blight), which are soil or seedborne for part of their life cycle. Since these infections can sometimes result in severe airborne epiphytics, they pose a particular problem for resistance control.

Frequent metalaxyl use in foliar applications for late blight control on potatoes have led to the establishment of a much more aggressive and competitive population of resistant isolates of *Phytophthora infestans* (late blight) in many parts of the world. Resistant isolates of *Peronospora vicae* also became evident following frequent use of metalaxyl in pea seed dressings for seedborne downy mildew control (Falloon et al 2000).

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# **Acknowledgments**

The funding of this project by Horticulture Australia Limited, Australian Potato Industry Council, and levies from vegetable industries, is gratefully acknowledged.

I would like to thank Dr. Doris Blaesing and Mary Trebilco of Serve-Ag Pty Ltd, and Dr. John Mathiessen of CSIRO Entomology, Western Australia, for their comments and proof-reading of the report.