WORLDWIDE DEVELOPMENT OF FIPRONIL INSECTICIDE

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Abstract

Fipronil is a member of a new family of insecticides called phenyl pyrazoles and was discovered in 1987 by Rhone-Poulenc scientists in the UK. Fipronil is a versatile insecticide for use in many different markets at low dose rates whilst providing high level efficacy against target insect pests. In its eight years of field evaluation and development, fipronil has been tested against more than 250 insect species on more than sixty crops worldwide. Fipronil is effective against a broad range of insect pests of various crops, including cotton, rice, sugarcane, bananas, potatoes, maize, sugar beet and sunflower. Dependent upon crop and target pests, fipronil can be used either for foliar or soil application and, because it is systemic, as a seed treatment. Fipronil is a potent blocker of the GABA (gamma-aminobutyric acid) regulated chloride channel, interfering with the central nervous system (CNS). Due to its mode of action, fipronil has proven highly effective in controlling insects resistant to commonly used insecticides, diamondback moth (Plutella xylostella) in particular. Fipronil is now registered in more than 30 countries for the control of a wide range of agricultural and non-agricultural pests.

Approximately 500 trials on cotton have been carried out since 1988. Trials programs have been established in Australia, Brazil, China, Colombia, Ecuador, El Salvador, Greece, Guatemala, Ivory Coast, Mexico, Malawi, Paraguay, Peru, Spain, USA, Venezuela and Zimbabwe. On cotton, fipronil is particularly effective against thrips, tarnished plant bugs, boll weevil and against agricultural termites. Good activity has also been demonstrated against leafworms, bollworms, budworms and borers. Fipronil is also very effective in the control of various non-crop pests. At this time fipronil is either commercialized or under development for the control of fleas and ticks on companion animals, flies and ticks on cattle, locusts, mosquitoes, and household insects such as cockroaches, ants and termites.

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Introduction

Fipronil is a novel insecticide belonging to a family of chemistry known as the phenyl pyrazoles (Figure 1). In eight years of laboratory and field trials, fipronil has been shown to be an extremely active compound, often requiring very low doses (5 - 150 g ai/Ha) to provide outstanding insect control. Depending upon crop and pest target, fipronil can be applied as a granule or soil spray, as a foliar spray, by seed treatment and as a bait. Fipronil was discovered by Rhone-Poulenc in 1987 and has been in worldwide development on major crops such as cotton, corn, rice, potato and vegetables, and for non-agricultural uses such as animal health, public health and locust control since 1989. The current registration status of fipronil is shown in Table 1.

Registered trade names for fipronil include: Regent®, Ascend®, Prince®, Cosmos®, LeSAK®, Presto®, Goliath®, Termidor®, Fourmidor® and Frontline®

Mode of Action and Resistance

Phenyl pyrazoles have been researched for many years by Rhône-Poulenc in order to better understand the relationship between structure and toxicity, both insecticidal and mammalian. Initial electrophysiology research with fipronil indicated it has an effect on the central nervous system (CNS). By conducting numerous *in vitro* assays, it has been concluded both by Rhône-Poulenc biochemists and independent researchers that fipronil interferes with the passage of chloride ions through the gamma-aminobutyric acid (GABA) regulated chloride channel, thereby disrupting CNS activity and, at sufficient doses, causing death. Furthermore, there is target site specificity between insects and mammals, with fipronil displaying tighter binding (i.e., higher potency) in the insect GABA chloride channel than in the vertebrate, providing useful selective toxicity.

This mode of action of fipronil sets it apart from most commercial insecticides presently on the market. While many classes of insecticides affect the CNS, they each have a unique receptor/enzyme on which they bind and exert their effect. Products in the pyrethroid and organochlorine classes are known to be agonists of the sodium channel, and the carbamate and organophosphate products are antagonists of the enzyme acetylcholinesterase. Imidacloprid is an antagonist of the acetylcholine receptor, and avermectins were recently reported to act on the glutamate receptor. Because of fipronil's specific interaction with the GABA receptor, there is good reason to consider fipronil as having a unique mode of action. In extensive laboratory bioassays and in biochemical/electrophysiological studies, fipronil shows no significant cross resistance with the established classes of insecticides, including cyclodiene insecticides like dieldrin that also act on the GABA system. After two years of field use, no change in fipronil's outstanding field performance against resistant insects has been seen. As fipronil distribution expands around the world, RP is committed to taking a proactive stance in maintaining resistance monitoring programs.

Physical and Chemical Properties

BSI Common Name:	Fipronil
Molecular Formula:	$C_{12}H_4Cl_2F_6N_40S$; Molecular Weight: 437.1
Melting Point:	195.5 - 203 ^{0}C
Vapor Pressure:	2.8 x 10-9 mm Hg (or 3.7 x 10^{-9} hPa)
Solubility:	In water 1.9-2.4 mg/1 at 20 ^{0}C
Density:	1.477- 1.626 at 20 ^{0}C (g/ml)
Flash Point:	Not flammable
Octanol/Water Partition Coefficient: LOG $P_{o/w}$ = 4.00	
Henry's Constant:	3.7 x 10^{-10} atm m^3 mol^{-1}

Mammalian Toxicology

Acute Oral LD_{50} (rats) 97 mg/kg body weight	
Acute Dermal LD_{50} (rats)	>2000 mg/kg body weight
Acute Dermal LD_{50} (rabbits	354 mg/kg body weight
Acute Inhalation LC_{50} (rats)	0.682 mg/l (4 hr. nose only)
Skin Irritation (rabbits)	Minimal
Eye Irritation (rabbits)	Moderate

Fipronil is not a skin sensitizer.
Fipronil is not mutagenic or teratogenic.
Fipronil does not represent an increased cancer risk for humans.
Fipronil has no effect on fetal development or reproductive performance.

Avian Toxicity

Fipronil has been extensively studied in a number of avian species. Gallinaceous birds exhibit a higher sensitivity to fipronil than do waterfowl and passerines (Table 2). Based upon results of acute and sub-acute toxicity studies, fipronil is considered as toxic to birds in the Galliformes family and non-toxic to other avian species. Fipronil does not adversely affect reproduction in avian species.

In palatability studies conducted with diets containing fipronil treated granules or fipronil treated seeds, birds evidenced an aversion to fipronil treated substrates, even in no-choice situations. Fipronil appears to have a reduced palatability for birds, reducing the risk to sensitive avian species.

Aquatic Toxicity

The toxicity of technical grade fipronil to a variety of aquatic species has been extensively studied under laboratory conditions (Table 3). Based upon results from laboratory studies on various species of fish and freshwater invertebrates, fipronil is considered highly toxic to some aquatic species. However, these laboratory results, while indicating a potential hazard, do not represent the true bioavailability of fipronil under field conditions. Fipronil adheres tightly to soil and has low solubility in water, as do its environmental degredates. Therefore the risk of the chemical entering a water body in dissolved (i.e., bioavailable) form via run-off is low. In several years of use, the application of fipronil to rice paddies at the low rates needed to control target pests has not caused adverse effects to beneficial aquatic organisms.

Metabolism

Fipronil is metabolized in plants, soil and animals via reduction, oxidation and/or hydrolysis. The three consistent metabolic products are the sulfone, the sulfide and amide, regardless of the biological system. The sulfone and sulfide are known to cause toxic effects similar to the parent while the amide does not. On plants treated by foliar application, photodegradation products are also observed.

Crop Residues

As a general rule, residues are low to non-detectable in crops treated with fipronil.

Environmental Impact

Fipronil is non-toxic to earthworms, soil microorganisms and aquatic plants. Fipronil is toxic to bees and therefore foliar application of fipronil to plants should be made when bees are not foraging. In general, fipronil is softer on beneficial insects than many competitive products. Applied as a granule or seed treatment, fipronil presents little or no risk to beneficial insects and bees.

Fipronil and its metabolites show low soil mobility, so there is little potential for ground water contamination or movement from treated areas. In field soil dissipation studies, the half-life of fipronil applied via soil incorporation ranged from 3 to 7.3 months with greater than 90% of residues remaining in the upper 30 cm of soil. Fipronil is degraded by sunlight.

In soil dissipation studies of fipronil applied to the soil surface, the half-life ranged from 0.7 to 1.7 months.

Formulations

Fipronil kills insects by contact and ingestion, the main path of activity being dependent on the specific insect target. Fipronil is also moderately systemic and in some crops can be used at low application rates to control insects by treatments in-furrow or to seeds. To obtain the most effective results for a given pest, Rhone-Poulenc scientists have formulated fipronil in a variety of ways for soil, foliar and seed treatment. These include micro granules, suspension concentrates, water dispersible granules, seed treatment and ultra low volume formulations (Table 4). No phytotoxicity has been observed in any of these formulations, even at exaggerated application rates.

Biological Activity - Worldwide Programs

Fipronil has been tested against more than 250 species of insect pests on more than 60 different crops worldwide. A summary of fipronil efficacy on a variety of crops is shown in Tables 5 a and b.

Performance on Cotton

Approximately 500 trials on cotton have been carried out since 1988. Trials programs have been established in Australia, Brazil, China, Colombia, Ecuador, El Salvador, Greece, Guatemala, Ivory Coast, Mexico, Malawi, Paraguay, Peru, Spain, USA, Venezuela and Zimbabwe. The major pest target for fipronil have been identified as boll weevil (Anthonomus spp.), tarnished plant bug (Lygus spp.) and thrips (Frankliniella spp. and Thrips tabaci) although fipronil is active on a wide variety of cotton insect pests (Table 5a). Figures 2 - 13 present some of the results from these trials on cotton.

Summary

In worldwide development programs, fipronil has demonstrated potential for use in numerous crops, including cotton, and against a broad spectrum of insect pests. The major strengths of fipronil include:

Broad spectrum activity
Unique chemistry and mode of action
Excellent fit in resistance management programs
Good soil and foliar persistence
Low use rates with reduced environmental hazard
Excellent crop tolerance
Formulation and application method flexibility
Limited mobility in soil
Systemic activity

Acknowledgments

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Table 1. Current registration status of fipronil.

Crop	Country of Registration
Cotton	Colombia, Guatemala, Peru, Paraguay, Brazil, Venezuela, Ecuador
Rice	Philippines, Indonesia, Thailand, Vietnam, China, Brazil
Banana	Cameroon, Ivory Coast, FWI, Ecuador, Windward Islands, France
Citrus	South Africa, Thailand, Ecuador
Corn	Zimbabwe, France, Mexico, US (EUP)
Sugarcane	Brazil, Zimbabwe, Honduras
Potato	Romania, Peru, Brazil, Ecuador
Soybean	Paraguay, Ecuador
Sugar beet	France
Sunflower	France
Watermelon	Thailand
Coffee	Ecuador
Brassicas	Ecuador, Indonesia, Philippines, China, Peru, Honduras, Malaysia
Alfalfa	Ecuador
PCO	France
Animal Health	> 30 countries, mostly Europe

Table 2. Acute toxicity of fipronil to avian species

SPECIES	STUDY	EFFECT LEVEL
Bobwhite quail	Acute LD50	LD50=11.3 mg/kg
Bobwhite quail	Sub-acute LC50	LC50=48 ppm NOEC=19.5 ppm
Pheasant	Acute LD50	LD50=31 mg/kg
Red-legged partridge	Acute LD50	LD50=34 mg/kg NOEL=16 mg/kg
House sparrow	Acute LD50	LD50=1120 mg/kg
Pigeon	Acute LD50	LD50>2000 mg/kg
Mallard duck	Acute LD50	LD50>2150
Mallard duck	Sub-acute LC50	LC50>5000 ppm NOEC=1250 ppm

Table 3. Toxicity of fipronil to aquatic species

SPECIES	STUDY	EFFECT LEVEL
Bluegill sunfish	Acute LC50 (96 hr)	LC50=85 µg/l NOEC=43 µg/l
Rainbow trout	Acute LC50 (96 hr)	LC50=248 µg/l NOEC=33.8 µg/l
European carp	Acute LC50 (96 hr)	LC50=430 µg/l NOEC=73 µg/l
Rainbow trout	Early life-stage toxicity NOEC (60 d post-hatch)	NOEC=15 µg/l MATC=20 µg/l
Daphnia magna	Acute EC50 (48 hr)	EC50=190 µg/l NOEC=52 µg/l
Daphnia carinata	Acute LC50 (48 hr)	LC50=3800 µg/l
Daphnia magna	Chronic NOEC (21 d)	NOEC=9.8 µg/l*
Duckweed	Chronic toxicity (14 d)	EC50>0.16 mg/l
Freshwater green alga *(Selenastrum capricornutum)*	Chronic toxicity (120hr)	EC50>0.14 mg/l
Freshwater blue alga *(Anabaena flos-aquae)*	Chronic toxicity (120hr)	EC50>0.17 mg/l
Green alga (*Scenedesmus subspicatus*)	Chronic toxicity (96 hr)	EC50=0.068 mg/l
Freshwater diatom	Chronic toxicity (120 h)	EC50>0.12 mg/l

*based upon effects on growth; the NOEC is 20 µg/l if based upon survival and reproduction data

Table 4. Most frequently used formulations of fipronil

Trade Names	Concentration	Formulation Type
REGENT'®50 SC	50 g/l	suspension concentrate
ASCEND® 50 SC	50 g/l	suspension concentrate
REGENT® 200 SC	200 g/I	suspension concentrate
REGENT® 800 WG	800 g/kg	water dispersible granule
REGENT® 1 GR	I g/kg	micro granule
REGENT® 3 GR	3 g/kg	micro granule on sand base
REGENT® 5 G R	5 g/kg	micro granule on clay base
REGENT® 15 GR	15 g/kg	micro granule on clay base
REGENT® 20 GR	20 g/kg	micro granules on clay base
REGENT UL 12.5®	12.5 g/l	Ultra Low Volume
REGENT UL 25®	25 g/l	Ultra Low Volume
REGENT® 250 FS	250 g/I	seed treatment / suspension concentrate
REGENT® 500 FS	500 g/I	seed treatment / suspension concentrate
TERMIDOR®	25 g/I	emulsifiable concentrate
GOLIATH®	0.05 g/kg	bait

Table 5a. Performance of fipronil in worldwide development programs
F = foliar, ST = seed treatment, G = granule, SS = soil spray, W = whorl

Crop	Binomial	Field rate	Appl. Method
Alfalfa	*Empoasca* spp.	100 g ai/Ha	F
	Hypera postica	15-30 g ai/Ha	F
Banana	*Cosmopolites sordidus*	0.1-0.5 g ai/plant	G, SS
Cereals	*Agriotes* spp.	50 g ai/ton	ST
	Delia coarctata	500 g ai/ton	ST
	Eurygaster integriceps	20 g ai/Ha	F
	Oelima melanopa	25 g ai/Ha	F
Chili	*Thrips palmi*	12.5-37.5 g ai/Ha	F
Citrus	*Phyllocnistis citrella*	4-8 gai/hl	F
	Scirtothrips aurantii	1-3 gai/hl	F
	Scirtothrips dorsalis	1-3 gai/hl	F
Coffee	*Hypothenemus hampei*	40-100 g ai/Ha	F
Corn	Termitidae	100 g ai/Ha	ST, SS, G
	Agriotes spp./*Limonius* spp.	100-150 g ai/Ha	ST, SS, G
	Atherigota spp.	50-150 g ai/Ha	ST, SS, G
	Chilo agamemnon	250-500 g ai/ton	ST
	Diabrotica virgifera	100-200 g ai/Ha	TB, SS, G
	Elasmopalpus lignosellus	250-500 g ai/Q	ST
	Helicoverpa armigera	100 g ai/Ha	F
	Oscinella frit	50-150 g ai/Ha	ST
	Ostrinia nubilalis	30-120 g ai/Ha	ST, G, SS, W
	Phyllophaga spp.	150-200 g ai/Ha	G
	Tanymechus dilaticollis	1.25-3.75 kg ai/ton	ST
Cotton	*Alabama argillacea*	2.5-50 g ai/Ha	F
	Anthonomus spp.	25-100 g ai/Ha	F
		50-100 g ai/Ha	F
	Eutinobothrus spp.	40 g ai/Ha	SS
	Thysaniptera	12.5-50 g ai/Ha	ST, G, F
	Heliothis spp.	50-300 g ai/Ha	F
	Lygus lineolaris	15-55 g ai/Ha	F
	Pectinophora gossypiella	50-200 g ai/Ha	F
	Polyphagotarsonemus latus	100-200 g ai/Ha	F
	Spodoptera spp.	50-200 g ai/Ha	F
	Termitidae	90-120 g ai/Ha	ST, SS
Crucifers	*Pieris* spp.	25 g ai/Ha	F
	Plutella xylostella	12.5-50 g ai/Ha	F
	Trichoplusia ni	25-50 g ai/Ha	F
Eggplant	Thysanoptera	25-37.5 g ai/Ha	F
Grapevine	*Clysia ambiguella*	50-100 g ai/Ha	F
	Lobesia botrana	50-100 g ai/Ha	F
	Scaphoideus titanus	50-100 g ai/Ha	F
	Sparganothis pilleriana	50-100 g ai/Ha	F
Grasshopper	*Melanoplus* spp.	1-10 g ai/Ha	F, B
Leek	*Hylemia antiqua*	40-100 g ai/Ha	ST
	Thrips tabaci	25-100 g ai/Ha	F, SD, ST
Mango	*Scirtothrips dorsalis*	12.5-25 g ai/Ha	F
Mushroom	Cecids, Phorids, Sciarids	3.2g/300 l casing	F, G
Oilseed Rape	*Phyllotreta* spp.	5 g ai/Kg seed	ST
	Psylloides spp.	50-100 g ai/Ha	ST
Ornamentals	*Frankliniella occidentalis*	25-100 g ai/Ha	F
Pasture	*Costelytra zealandica*	75-200 g ai Ha	G, ST
Peanuts	*Frankliniella* spp.	25-50 g ai/Ha	SS
Pea	*Sitona lineatus*	25-50 g ai/Ha	F, ST

Table 5b. Performance of fipronil in worldwide development programs
F = foliar, ST = seed treatment, G = granule, SS = soil spray, W = whorl

Crop	Binomial	Field rate	Appl. Method
Pepper	*Anthonomus eugenii*	25 g ai/Ha	F
Potato	*Graphognathus* spp.	50-150 g ai/Ha	SS
	Agriotes spp.	100 g ai/Ha	G, SS
	Diabrotica speciosa	100 g ai/Ha	SS
	Empoasca favae	100 g ai/Ha	F
	Leptinotarsa decemlineata	10-30 g ai/Ha	F
	Limonius spp.	100 g ai/Ha	G, SS
	Thysanoptera	25-50 g ai/Ha	F
Radish	*Phyllotreta striolata*	25-100 g ai/Ha	F
	Psylloides punctifrons	25-100 g ai/Ha	F
Rice	*Aphelnoides* spp.	25-100 g ai/Ha	G, ST
	Chilo suppressalis	25-50 g ai/Ha	F, G, ST
	Cnaphalacrosis spp.	25-50 g ai/Ha	F, G, ST
	Frankliniells spp.	10-25 g ai/Ha	F, G, ST
	Hydrellia griseola	25-50 g ai/Ha	F, G, ST
	Laodelphax striatellus	25-75 g ai/Ha	F, G, ST
	Leptocorsica spp.	25-50 g ai/Ha	F, G, ST
	Lissorhoptrus spp.	25-75 g ai/Ha	F, G, ST
	Cicadellidae	50-150 g ai/Ha	F, G, ST
	Nilaparvata lugens	25-75 g ai/Ha	F, G, ST
	Nymphula spp.	25-50 g ai/Ha	F, G, ST
	Oebalus poecilus.	25-50 g ai/Ha	F, G, ST
	Oelema oryzae	25-50 g ai/Ha	F, G, ST
	Rupela albinella	25-75 g ai/Ha	F, G, ST
	Sogatella furcifera	25-75 g ai/Ha	F, G, ST
	Susamia spp.	25-75 g ai/Ha	F, G, ST
	Thrips spp.	25-50 g ai/Ha	F, G, ST
	Tryporyza spp.	25-50 g ai/Ha	F, G, ST
Sorghum	*Blissus leucopterus*	25-100 g ai/Ha	SS, F
	Chilo spp.	200 g ai/Ha	F
Soybean	*Anticarsia gemmatalis*	40-80 g ai/Ha	F
	Piezodorus guildini	80-100 g ai/Ha	F
Sugar Beet	*Agriotes* spp.	100-150 g ai/Ha	G, ST
Sugarcane	*Aeneolamia saccharina*	50-100 g ai/Ha	F
	Chilo infuscatellus	50-200 g ai/Ha	G, SS
	Termitidae	50-200 g ai/Ha	G, SS
Sunflower	*Agriotes* spp.	100-150 g ai/Ha	G, ST
Tea	Tortricidae	100 g ai/Ha	F
	Scirtothrips dorsalis	25-50 g ai/Ha	F
Tobacco	*Epitrix hirtipennis*	25-50 g ai/Ha	F
	Heliothis virescens	100 g ai/Ha	F
	Manduca sexta	100 g ai/Ha	F
Top Fruit	*Cydia molesta*	50 g ai/Ha	F
	Conotrachelus nenuphar	50-100 g ai/Ha	F
	Cydia pomonella	50-200 g ai/Ha	F
	Hoplocampa testudinea	50-100 g ai/Ha	F
	Leucoptera scitella	50-150 g ai/Ha	F
	Tortricidae	50-100 g ai/Ha	F
	Psylla spp.	50-150 g ai/Ha	F
	Typhlocba pomaria	50-200 g ai/Ha	F
Watermelon	*Haplothrips floricola*	25-37.5 g ai/Ha	F

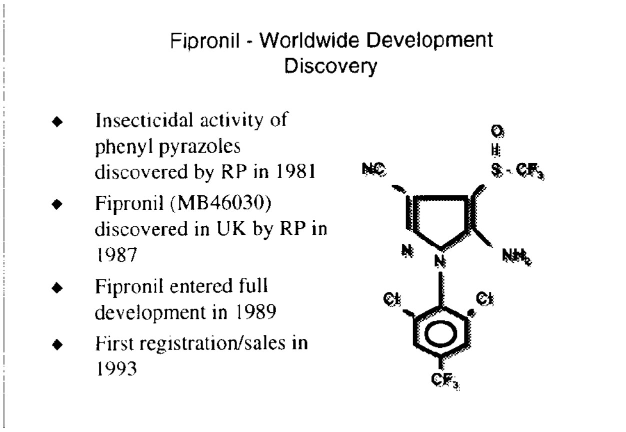

Figure 1. Structure and discovery of fipronil.

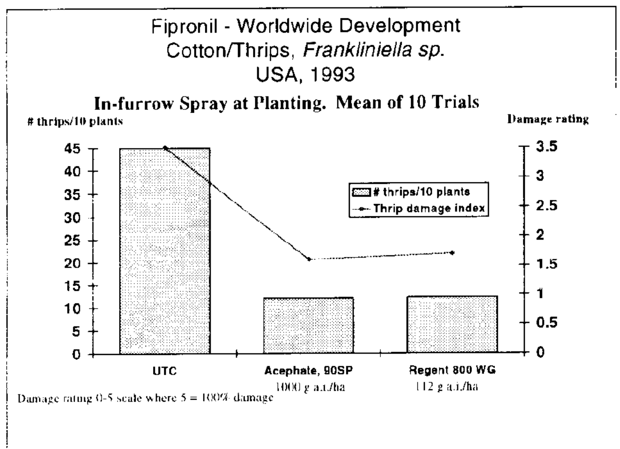

Figure 2. Control of Frankliniella spp. on cotton with an in-furrow application of fipronil at planting.

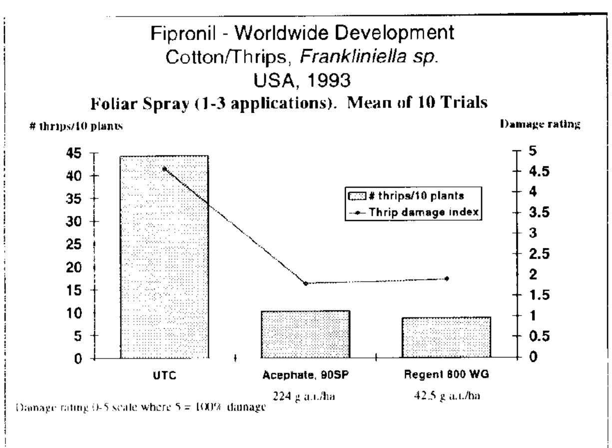

Figure 3. Control of Frankliniella spp. on cotton with a foliar spray of fipronil.

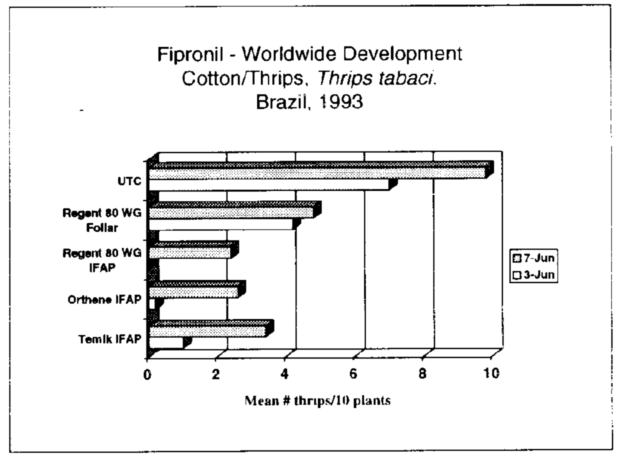

Figure 4. Control of Thrips tabaci on cotton with an in-furrow spray of fipronil at planting and by foliar spray.

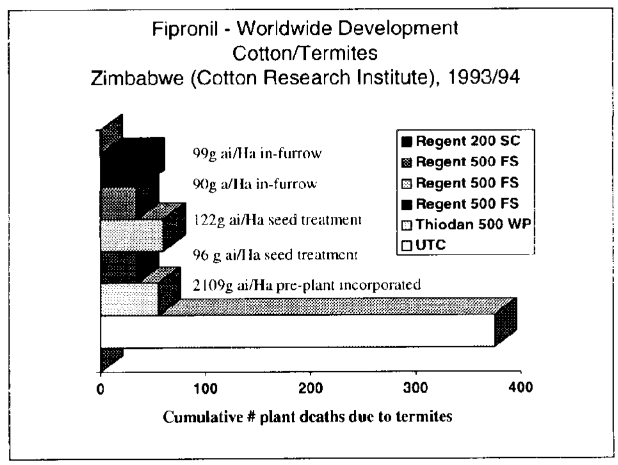

Figure 5. Control of agricultural termites on seedling cotton using fipronil as an in-furrow sprays or seed treatment at planting.

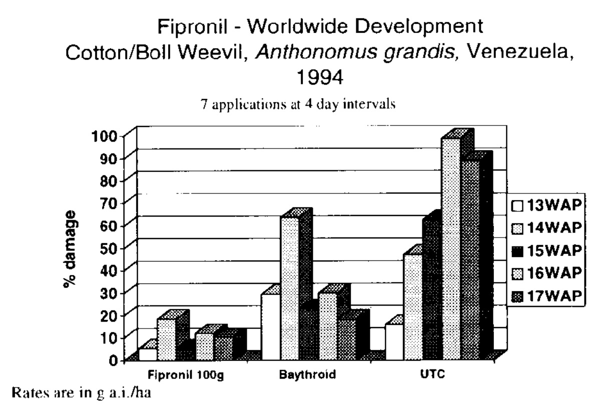

Figure 6. The activity of fipronil on Anthonomus grandis in Venezuela in a seven application foliar spray program.

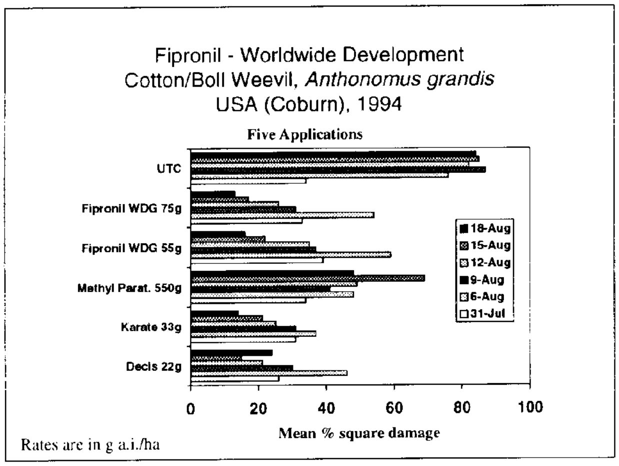

Figure 7. The activity of fipronil on Anthonomus grandis in a 1994 trial in the USA in a five application foliar spray program.

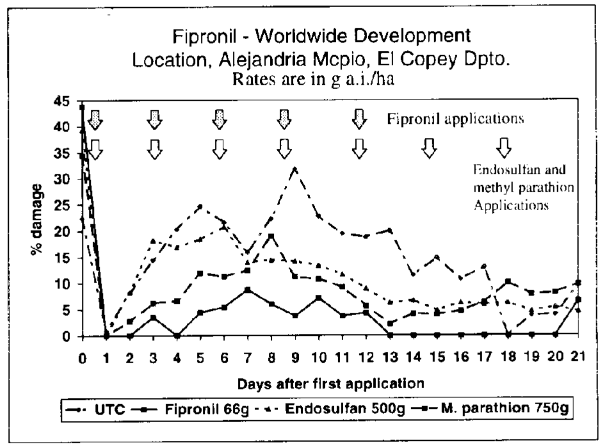

Figure 10. A comparison of the efficacy (measured as the percentage of damaged fruit) of fipronil, endosulfan and methyl parathion against boll weevil in a season long spray program; Colombia, 1991.

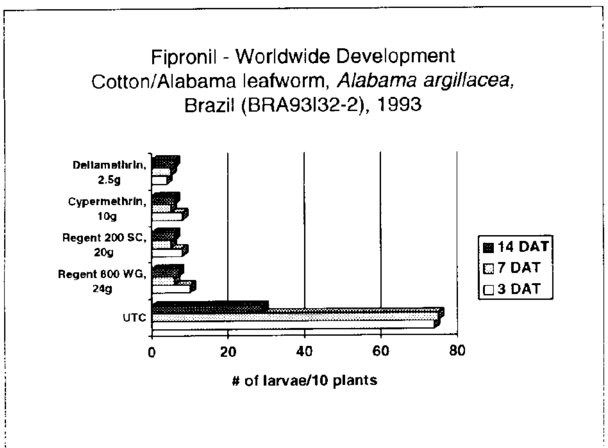

Figure 8. The efficacy of a foliar application of fipronil on Alabama argillacea on cotton in Brazil

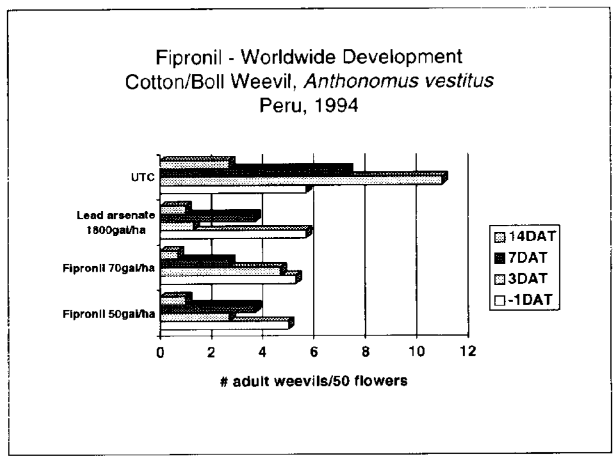

Figure 11. The activity of fipronil applied as a foliar spray on Anthonomus vestitus in Peru.

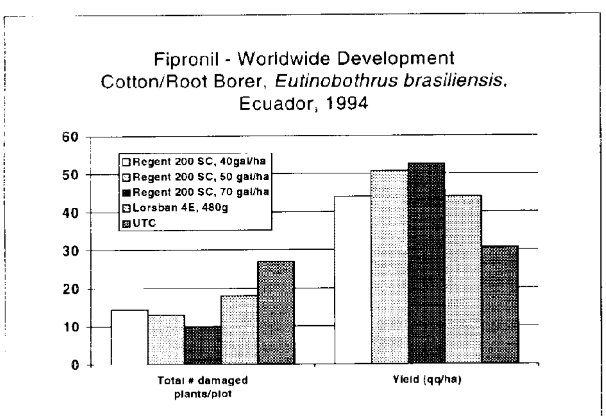

Figure 9. The activity of fipronil against the cotton root borer. Eutinobothrus brasiliensis in Ecaudor. Fipronil was applied as a spray at the base of the plant.

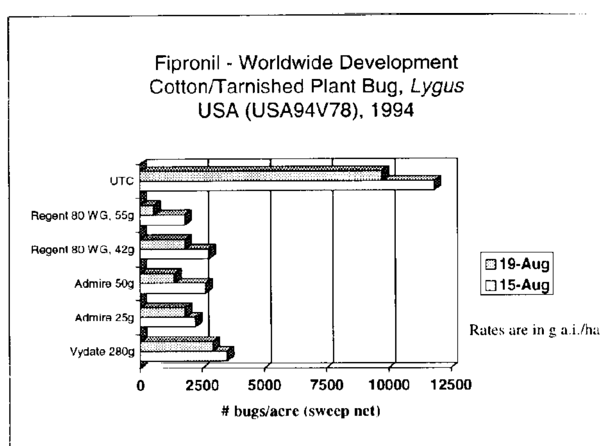

Figure 12. Control of the tarnished plant bug, Lygus spp. on cotton in the USA using a foliar application of fipronil.

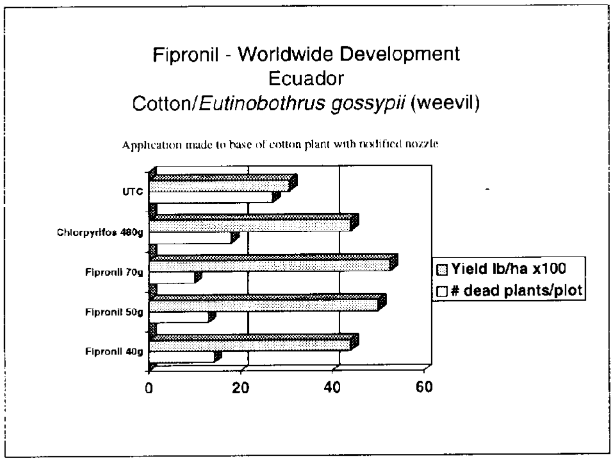

Figure 13. Control of Eutinobothrus gossypii in Ecuador using a modified nozzle to spray the base of the plant.