Technical Update

Standards including

Fipronil

Fipronil Metabolites

Oxychlordane

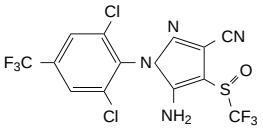
o,p'-Methoxychlor

Pesticides and Their Metabolites

Without pesticides the world would not be able to feed as many people as it does. With pesticides, there have been a multitude of health effects, including death. The bridge between these two ends of the spectrum is in understanding. That understanding comes from research into pesticides, including research into the products or metabolites that pesticides convert in the environment.

Fipronil and Its Metabolites: An Example

In recent years, there has been much discussion about the toxicity of Fipronil. Along with the discussion of Fipronil, there came even more discussion about its metabolites: Fipronil Sulfide, Fipronil Sulfone, and Fipronil Desulfinyl (1). Fipronil is a member of the phenyl pyrazole class of pesticides. It is a highly effective, broad-spectrum insecticide with potential value for control of a wide range of crop, public hygiene, amenity and veterinary pests. It can be applied at low to very low dose rates to achieve pest control (2). Fipronil, as the parent compound, is classified as a World Health Organization (WHO) Class II moderately hazardous pesticide. It is neurotoxic, that is, it disrupts normal nerve function (6) in both rats and dogs, and is carcinogenic to male rats at 300 mg/kg, where the LD50 (the dose required to kill half a population of lab animals) is 97 mg/kg (4). Fipronil is used in Frontline flea and tick products such as Top Spot and Spray treatment (5) for cats and dogs, but at low levels that at worst, have been found to result in skin irritation and/or hair loss at the site of application (1,2,3). These formulated products are not absorbed through the skin and have low toxicity if ingested (3,6). In laboratory studies, it has been found that Fipronil has a half-life of 122-128 days in oxygenated sandy loam soil, while in field studies, it ranged from 0.7 days to 1.7 months (3). Fipronil has been found to degrade slowly by anaerobic metabolism in the soil, resulting in the metabolite known as Fipronil Sulfide (1,3). It can undergo photodegradation, resulting in the metabolite Fipronil Desulfinyl (1,3). When it degrades in the soil under oxidative conditions, it results in the metabolite Fipronil Sulfone (1). Because it binds to the soil, Fipronil and its metabolites have a low potential for groundwater contamination (1,3,6) and have not been found to be volatile in nature (1). However, the metabolites have been determined to be much more toxic to various organisms than the parent compound, Fipronil. Fipronil Sulfide is more toxic than Fipronil to freshwater invertebrates, while Fipronil Sulfone is more toxic to avian species and freshwater fish and invertebrates (6). Fipronil Desulfinyl is generally more toxic to a variety of animals while being very persistent in the environment (8).

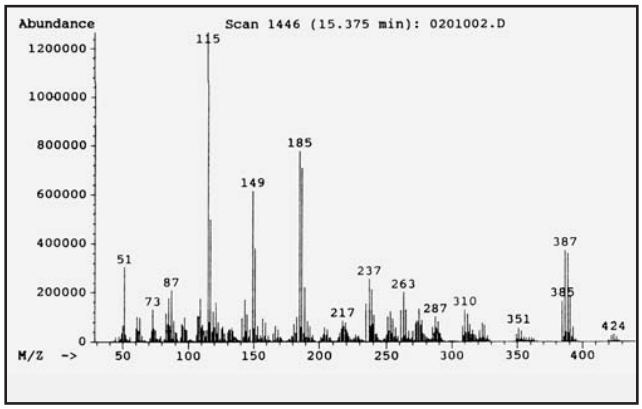


Fipronil & Metabolite Kit

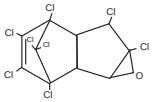
P-FIP-MET-KIT *(All in 100 µg/mL in MeOH, except Fipronil in Acetone)*			**4 x 1 mL**
P-738S-A	**Fipronil**	P-781S	**Fipronil sulfide**
P-780S	**Fipronil sulfone**	P-782S	**Fipronil desulfinyl**

Oxychlordane: A Metabolite of Chlordane

Oxychlordane is an organochlorine compound that is the most persistent metabolite of Chlordane (7,8). It is bioaccumulative and is one of the most toxic of the chlordane compounds (7,9). Because of its toxicity and ability to bioaccumulate, it was banned in the United States in 1988 (11), banned in 47 other countries and severely restricted in 14 others (10). Even though it has been 15 years since the ban has been implemented, chlordane can still be detected in some foods grown in the United States (10). Chlordane has been used on corn and citrus crops, and on residential lawns and gardens (8,10). One of its most common uses was as a pesticide for termites (8,10). Chlordane is potentially volatile but is capable of binding to sediment in water and soil (8). If it binds to sediment in water or soil, the degradation process can be very slow, taking potentially up to 20 years (8,10). Since chlordane can bind itself to sediment in water, fish and shellfish are especially susceptible to ingesting the chemical. Humans become exposed to high doses of chlordane through consuming the fish that have already bioaccumulated it. "Other less significant routes of exposure may include eating crops grown in soil containing chlordane; breathing air or touching soil near homes treated for termites with chlordane; and breathing air or touching soil near waste sites or landfills. The seriousness of these minor routes depends on the extent of the chlordane contamination, but significantly, none of them involve bioaccumulation" (10). Once ingested, some of the chlordane is excreted within several days (8,10).



Oxychlordane
2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2H-indeno(1,2,b)oxirene
CAS No. 27304-13-8



$C_{10}H_4Cl_8O$
M.W. = 420

Oxychlordane formulations available

Description	Conc. / Solvent (1 mL)	Cat. No.
Oxychlordane	10 µg/mL in MeOH	P-331S-0.1X
Oxychlordane	100 µg/mL in MeOH	P-331S
Oxychlordane	100 µg/mL in Hexane	P-331S-H

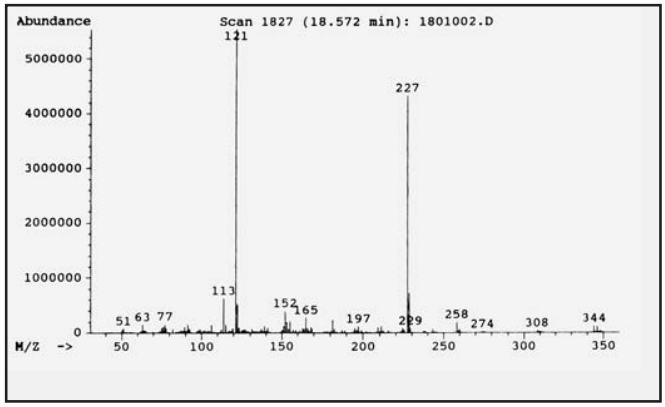
AccuStandard®
Standards are our Life
www.accustandard.com

125 Market St.
New Haven, CT 06513
800.442.5290
203.786.5290

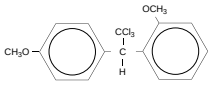
The chlordane that remains in the body is converted to the toxic metabolite in a mammal's liver and gets stored in adipose tissue as chlordane metabolites: quite often oxychlordane (12). The oxychlordane stored in this adipose tissue can take years before leaving the body. Another way in which the oxychlordane leaves the body is through mother's breast milk or across the placenta in utero (12).

Methoxychlor: Another Alternative

Methoxychlor is an organochlorine that has been increasingly used since 1972, when the ban of DDT was set in place. With a relatively low toxicity and relatively low persistence in the biological system, it has been found to be an excellent replacement for DDT (11,12). Methoxychlor is effective against pests that are found in agriculture, residences, and residential plantings. Methoxychlor has been used on vegetables, fruits, forage crops, DDT-sensitive crops such as squash, melons, etc. (13) and in forestry as well as to kill parasites on dairy and beef cattle (13). Canada has implemented its usage for the control of biting flies (14). It has been found to be very persistent in soil with a half-life of 120 days without the presence of oxygen. With the presence of oxygen in soil, the half-life can be as little as 1 week. As it is insoluble in water, it is not likely to contaminate groundwater. However, because there have been low levels detected in ground and surface water, the mechanism is believed to have entered the water as the result of high levels of rain, an excessive amount applied to the soil or vegetation or it is believed to have bound to a soil particle and the soil particle enters the groundwater system (11,13). Studies have demonstrated that Methoxychlor does not accumulate in the body in adipose tissue or any other location in any significant amount. In a study conducted with mice, over 98% was excreted within 24 hours after a single dose. In an extended study occurring over 18 weeks, there was no Methoxychlor detectable in the body two weeks after study conclusion (11). It has been found to be slightly toxic to birds, highly toxic to fish and aquatic invertebrates and not toxic at all to bees (11).
Like technical DDT, technical Methoxychlor is composed of its para – para and ortho – para isomers. The Methoxychlor available from the usual Reference Material merchants is the para – para isomer. For environmental analysis, the ortho – para is also needed. AccuStandard synthesizes each of these.



o,p'-Methoxychlor
1,1,1-Trichloro-2-[o,p'-(dimethoxy phenyl)]ethane
CAS No. 30667-99-3



$C_{16}H_{15}Cl_3O_2$
M.W. = 344

o,p'-Methoxychlor formulations available

Description	Conc. / Solvent (1 mL)	Cat. No.
o,p'-Methoxychlor	100 µg/mL in MeOH	P-535S
o,p'-Methoxychlor	100 µg/mL in Isooctane	P-535S-TP
p,p'-Methoxychlor-olefin	100 µg/mL in MeOH	P-466S

AccuStandard

AccuStandard synthesizes the pesticides and metabolites in this article and many others shown in our catalog. They have the advanced technology, capabilities and knowledgeable chemists on staff that manufacture high quality neat products of pesticides. Additionally, with about 3,200 pesticides available in catalog and custom offerings, AccuStandard will exceed your laboratory's expectations as a Certified Reference Material Manufacturer.

References:

1. Tingle, C., Rother, J., Dewhurst,C., Lauer, S., King, W. Health and Environmental Effects of Fipronil. (2000) Retrieved January 21, 2004 from http://www.pan-uk.org/briefing/fipronil.pdf
2. Unknown. Fipronil. (2003) Retrieved January 23, 2004 from http://www.pan-uk.org/pestnews/actives/fipronil.htm
3. Unknown. Fipronil. (2002) http://ace.orst.edu/info/npic/factsheets/fipronil.pdf
4. WHO, Classification of Pesticides by Hazard 1998-1999, International Programme on Chemical Safety, WHO/IPCS/98.21.
5. Unknown. Frontline Brand Products. (2004) Retrieved January 23, 2004 from http://frontline.us.merial.com/faq/faq.asp
6. Madsen, J., Sandstrom, M., Zaugg,S. (2003) Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory – A Method Supplement for the Determination of Fipronil and Degradates in Water by Gas Chromatography/Mass Spectrometry: Open File Report 02-462.
7. Gladen, B., et al. Organochlorines in Breast Milk from Two Cities in Ukraine. (1999) Retrieved January 21, 2004 from http://ehp.niehs.nih.gov/members/1999/107p459-462gladen/ gladen-full.html
8. Federal Register on November 26, 1974, (39 F.R. 41298).PR Notice 74-11, Notice To Producers, Formulators, Distributors and Registrants of Pesticides, December 2, 1974 Retrieved Janurary 21, 2004 from http://www.pesticide.net/x/notice/epa/pr74-11.html
9. Bondy, G. Related Changes in Trans-Nonachlor, Trans-Chlordane and Oxychlordane Levels in Rat Tissues. (2003) Retrieved January 26, 2004 from http://www.ainc-inac.gc.ca/ncp/hhlth_e.html
10. Unknown. Healthy Milk Healthy Baby: Chemical Pollution and Mothers Milk (1999). http://www.nrdc.org/breastmilk/chem1.asp
11. Unknown. Methoxychlor (1996) Retrieved January 21, 2004 from http://ace.ace.orst.edu/info/extoxnet/pips/methoxyc.htm
12. Unknown. Methoxychlor (2003) Retrieved January 21, 2004 from http://www.epa.gov/ttnatw01/hlthef/methoxyc.html
13. Unknown. Consumer Factsheet on: METHOXYCHLOR. (1996) Retrieved January 21, 2004 from http://www.epa.gov/safewater/contaminants/dw_contamfs/methoxyc.html

Pesticide Standards as Neats, Low & High Concentration Solutions

Most solutions are in MeOH, Neats are 10 mg

Abamectin
Abate
a-BHC
Acephate
Acetochlor
a-Chlordane
a-Chlordene
Acifluorfen
Acifluorfen methyl ester
a-Cypermethrin
Alachlor
Alanap
Alar
Albendazole
Aldicarb
Aldicarb sulfone
Aldicarb sulfoxide
Aldrin
Allethrin
Allidochlor
Alloxydim-sodium
Aluminium phosphide
Ametryn
Aminocarb
Aminomethylphosphonic acid
Amitraz
Amitrole
Ammonium sulfamate
Ancymidol
Anilazine
Aramite
Aspon

Atrazine
Atrazine-desisopropyl
Atrazine-desisopropyl-2-hydroxy
Azaditrachtin
Azamethiphos
Azinphos ethyl
Azinphos methyl
Azocyclotin
Azoxystrobin
Barbamate
Barnon
Baycarb
Baycor
Baygon
b-BHC
Benalaxyl
Benazolin
Bendiocarb
Benfluralin
Benfuracarb
Benodanil
Benomyl
Benoxacor
Bensulfuron-methyl
Bensulide
Bensultap
Bentazon
Bentazon methyl derivative
Benzoylprop ethyl
BHC Tech
Bifenox
Bifenthrin
Binapacryl
Bioallethrin d-trans-allethrin

bis(Tributyltin)oxide
bis-2-Ethylhexyl adipate
Bitrex
Bloc
Bolstar
Bonzi
Botran
Brodifacoum
Bromacil
Bromadiolone
Brominal
Bromofenoxim
Bromophos-ethyl
Bromophos-methyl
Bromopropylate
Bromoxynil methyl ether
Bromoxynil octanoate
Bueno
Bupirimate
Buprofezin
Busan
Butachlor
Butocarboxim
Butocarboxim sulfoxide
Butralin
Buturon
Butylate
Cadusafos
Captafol
Captan
Carbaryl
Carbendazim
Carbetamide
Carbofuran
Carbofuran phenol

Carbophenothion
Carbosulfan
Carboxin
Cartap hydrochloride
Chinomethionate
Chloramben
Chloramben methyl ester
Chlorbenside
Chlorbromuron
Chlorbufam
Chlordane
Chlordene
Chlordimeform
Chlorfenvinphos
Chlorflurecol-methyl ester
Chlorflurenol
Chlorimuron ethyl
Chlormephos
Chlormequat chloride
Chlorobenzilate
Chloroneb
Chlorophacinone
Chloropicrin
Chloropropylate
Chlorothalonil
Chloroxuron
Chlorpropham
Chlorpyrifos-methyl ester
Chlorsulfuron
Chlorthiamid
Chlorthion
Chlorthiophos
Chlortoluron
Chlozolinate
Chorpyrifos-oxon

Clethodim
Clofentezine
Clomazone
Clopyralid methyl ester
Copper oxychloride
Coumachlor
Coumaphos
Coumatetralyl
Crimidin
Crufomate
Cyanazine
Cyanofenphos
Cyanophos
Cycloate
Cycloheximide
Cycloxydime
Cyfluthrin
Cyhexatin
Cymoxanil
Cypermethrin
Cyphenothrin
Cyprazine
Cyproconazole (Tech)
Cyprodinil
Cyromazine
Cythion
Dacthal
Dalapon acid
Dalapon methyl ester
Danitol
Dasanit
Dazomet
DBCP
d-BHC
DCMU
DCPA diacid

Omethoate
o-Phenylphenol
Orbencarb
Oryzalin
Ovex
Oxadiazon
Oxadixyl
Oxamyl
Oxycarboxin
Oxychlordane
Oxydemeton-methyl
Oxyfluorfen
p,p'-DDA
p,p'-DDD
p,p'-DDE
p,p'-DDT
p,p'-Methoxychlor-olefin
Paraoxon
Paraquat CL • 4H2O (as Paraquat)
Parathion
PCNB
PCP methyl ether
Penconazol
Pencycuron
Pendimethalin
Pentachloroanisole
Permethrine (cis/trans)
Perthane
Phenmedipham
Phenothiazine
Phenthoate
Phenyl mercury acetate
Phenyl valerate
Phorate
Phorate sulfone
Phorate sulfoxide
Phosalone
Phosfolan
Phosmetoxon
Phosphamidon
Phoxim
Picloram
Picloram methyl ester

Pirimicarb
Pirimphos-ethyl
Pirimphos-methyl ester
Potassium dimethyl dithiocarbamate
Prebane
Pretilachlor
Probenazole
Probenazole
Prochloraz
Procymidone
Prodiamine
Profenofos
Profluralin
Promecarb
Prometon
Prometryne
Pronamide
Propachlor
Propamocarb hydrochloride
Propanil
Propargite
Propazine
Propetamphos
Propham
Propineb
Prosulfocarb
Prothoate
Prtallethrin
Pyraclofos
Pyrazon
Pyrazophos
Pyrazoxyfen
Pyrethrins
Pyridaben

Pyriphenox
Pyroquilon
Queletox
Quinalphos
Quinclorac
Quizalofop ethyl
Resmethrin
Ronnel
Rotenone
S421 NEW
Schradan
Sebuthylazine
Secbumeton
Sethoxydim
Siduron
Silafluofen
Silvex
Silvex 2-ethylhexyl ester
Silvex methyl ester
Simazine
Simeton
Simetryn
Sodium diethyldithiocarbamate
Strobane
Sulfallate
Sulfometuron methyl ester
Sulfoquinoxaline
Sulfotep
Sulfoxide
Sumithrin
Swep
TCA
Tebuconazol
Tebufenozide
Tebupirimfos

Teflubenzuron
Tefluthrin NEW
TEPP
Terbacil
Terbufos
Terbufos sulfone
Terbufos sulfoxide
Terbumeton
Terbuthylazin-desethyl
Terbuthylazine
Terbutol
Terrazole
Tetrachlorvinphos
Tetraconazole
Tetradifon
Tetrahydro-phthalimide
Tetramethrin
Tetrasul
Thiabendazole
Thidiazuron
Thifensulfuron methyl
Thiobencarb
Thiocyclam hydrogen oxalate
Thiodicarb
Thiofanox
Thiofanox sulfoxide
Thiometon
Thionazin
Thiophanate
Thiophanate-methyl
Thiram
Tillam
Tilt
Tokuthion

Toxaphene
Tralkoxydim
Tralomethrin
Transfluthrin
trans-Nonachlor
Triadimefon
Triadimenol
Triallate
Triasulfuron
Triazophos
Tribenuron-methyl
Trichlorfon
Trichloronate
Triclopyr
Triclopyr methyl ester
Triclopyr-2-butoxy ethyl ester
Tricresyl phosphate
Tricyclazole
Tridemorph
Trietazine
Triethylphosphate
Trifenmorph
Triflumizole
Triflumuron
Trifluralin
Triforine
Trimethyl phosphate
Trimidal
Triphenyl phosphate
Vacor
Vamidithion
Vanicide-20S
Vernolate
Vinclozolin
Warfarin
Zinc Phosphide
Zineb
Ziram
Zolone

For a complete listing of over 3,200 pesticide standards (A to Z), visit our website at www.accustandard.com or call us at 203-786-5290.

AccuStandard®
Standards are our Life
www.accustandard.com

125 Market St.
New Haven, CT 06513
800.442.5290
203.786.5290

BO4-3000