Current Methods of Analysis for Selected Herbicides, Insecticides, Antibiotics, Taste-and-Odor Problems, and Their Degradation Products

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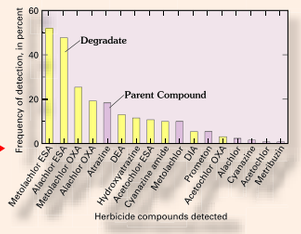
Organic Geochemistry Research Group

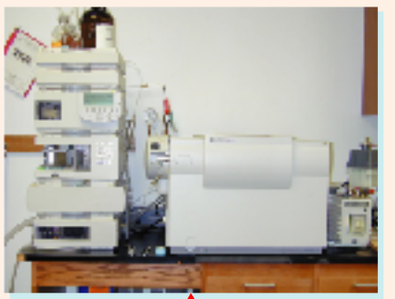
In 1987, the Organic Geochemistry Research Group was established at the U.S. Geological Suevey (USGS) district office in Lawrence, Kansas, to investigate the fate, degradation, and transport of agricultural chemicals in surface and ground water. The goals and accomplishments of the research group are as follows: (1) To develop analytical methods: Accomplishments include three official methods that have been approved by the USGS Office of Water Quality. (2) To investigate the occurrence, quality, and movement of herbicides, insecticides, antibiotics, taste-and-odor problems, and degradation products in surface and ground water throughout the United States: Accomplishments include water-quality surveys of surface water, rainfall, storm events, ground water, reservoirs, the Mississippi River flood, atrazine label study, tile drains in the Midwest, and confined animal feeding operations. Special projects include studies of mosquito insecticides in New York City, and pharmaceuticals in surface water of the United States. (3) To study the degradation, transport, and fate of agricultural chemicals in the hydrologic environment: Accomplishments include the findings of formation and transport of deethylatrazine in the soil and vadose zone, dissipation of encapsulated herbicides, understanding regional transport of herbicides and their degradation products in surface water, effects of pesticides on frogs, and taste-and-odor problems related to drinking water and algal production. The research group has produced an extensive bibliography of over 100 scientific publications including 4 books, 52 journal articles, 34 USGS publications, 18 chapters and proceedings, and 11 university theses.

The Importance of Degradation Products!

Although numerous studies have been conducted investigating the occurrence of herbicides in ground water, few have considered the degradation products of these herbicides. The figure at right shows the frequency of detections of parent/degradation products from municipal wells in Iowa sampled during 1996 (courtesy of D.W. Kolpin, USGS, Iowa).



Gas chromatography/mass spectrometry (GC/MS)



Liquid chromatography/mass spectrometry (LC/MS)

Enzyme-linked immunosorbent assay (ELISA)

Methods of Analysis for Herbicides, Insecticides, Antibiotics, Taste-and-Odor Problems, and Degradation Products

Compound	Type	Class	GC/MS	LC/MS	ELISA
Acetochlor	H	ACET	x		
Acetochlor ESA	H,DP	ACET DP		x	
Acetochlor OXA	H,DP	ACET DP		x	
Alachlor	H	ACET	x		
Alachlor ESA	H,DP	ACET DP		x	
Alachlor OXA	H,DP	ACET DP		x	
alpha-HCH	I	OC	x		
Ametryn	H	TRI	x		
AMPA (amino methyl phosphonic acid)	H,DP	OPH DP		x	
Atrazine	H	TRI	x	x	x
Azinfos ethyl	I	OP	x		
beta-HCH	I	OC	x		
Carbadox	A	Q		x	
Carbophenothion	I	OP	x		
Chlorfenvinfos	I	OP	x		
Chlortetracycline	A	TC		x	
Chlorpyrifos	I	OP	x		
Chlorpyrifos methyl	I	OP	x		
cis Chlordane	I	OC	x		
Coumafos	I	OP	x		
Cyanazine	H	TRI	x	x	x
Cyanazine acid	H,DP	TRI DP		x	
Cyanazine amide	H,DP	TRI DP	x	x	
DCA (3,4-dichloroaniline)	H,DP	PU DP		x	
DCPMU (3,4-dichloromethylphenylurea)	H,DP	PU DP		x	
DCPU (3,4-dichlorophenylurea)	H,DP	PU DP		x	
Deethylatrazine	H,DP	TRI DP	x	x	
Deethylcyanazine	H,DP	TRI DP		x	
Deethylcyanazine acid	H,DP	TRI DP		x	
Deethylcyanazine amide	H,DP	TRI DP		x	
Deethylhydroxyatrazine	H,DP	TRI DP		x	
Deisopropylatrazine	H,DP	TRI DP	x	x	
Deisopropylhydroxyatrazine	H,DP	TRI,DP		x	
Deisopropylprometryn	H,D	TRI,DP	x		
delta-HCH	I	OC	x		
Demethylnorflurazon	H,DP	PDZ DP	x		
Diazinon	I	OP	x	x	
Dioxazon	I,DP	OP,DP			
Dichlorvos	I	OP	x		
Dicrotofos	I	OP	x		
Didealkylatrazine	H,DP	TRI DP		x	
Dieldrin	I	OC	x		x
Dimethenamid	H	ACET	x		
Dimethenamid ESA	H,DP	ACET DP		x	
Dimethenamid OXA	H,DP	ACET DP		x	
Diuron	H	PU		x	
DMFM (demethylfluometuron)	H,DP	PU DP	x	x	
Doxycycline	A	TC		x	
Endosulfan I	I	OC	x		
Endosulfan II	I	OC	x		
Endosulfan sulfate	I,DP	OC DP	x		
Endrin	I	OC	x		
Endrin aldehyde	I,DP	OC DP	x		
Endrin ketone	I,DP	OC DP	x		
Ethion	I	OC	x		
Ethoprop	I	OP	x		
Fenchlorofos	I	OP	x		
Fenitrothion	I	OP	x		
Fensulfothion	I	DP	x		
Fenthion	I	OP	x		
Flufenacet	H	ACET	x		
Flufenacet ESA	H,DP	ACET DP		x	
Flufenacet OXA	H,DP	ACET DP		x	
Flumequine	A	Q		x	
Fluometuron	H	PU	x	x	x
Fonofos	I	OP	x		
gamma-HCH/Lindane	I	OC	x		
Geosmin	TO	ODOR	x		
Glyphosate	H	OPH		x	x
Glufosinate	H	OPH		x	
Heptachlor	I	OC	x		
Heptachlor epoxide	I,DP	OC DP	x		
Hydroxyatrazine	H,DP	TRI DP		x	
Leptofos	I	OP	x		
Linuron	H	PU		x	
Malathion	I	OP	x		
Merphos	I	OP	x		
Methidathion	I	OP	x		
Methoprene	I	IGR	x		
Methoprene acid	I,DP	IGR DP			x
Methoxychlor	I	OC	x		
MIB (2-methylisoborneol)	TO	ODOR	x		
Methyl parathion	I	OP	x		
Metolachlor	H	ACET	x		x
Metolachlor ESA	H,DP	ACET DP		x	
Metolachlor OXA	H,DP	ACET DP		x	
Metribuzin	H	TRI	x		x
Mevinphos	I	OP	x		
Minocycline	A	TC		x	
Molinate	H	TH	x		
Monocrotofos	I	OP	x		
Norfloxacin	A	Q		x	
Norflurazon	H	PDZ	x		
Oxolinic acid	A	Q		x	
Oxytetracycline	A	TC		x	
Parathion	I	OP	x		
Pendimethalin	H	DNA	x		
PBO (piperonyl butoxide)	I	SYN	x		
p,p'-DDD	I,DP	OC DP	x		
p,p'-DDE	I,DP	OC DP	x		
p,p'-DDT	I	OC	x		
Prometon	H	TRI	x		
Prometryn	H	TRI	x		
Propachlor	H	ACET	x		
Propachlor ESA	H,DP	ACET DP		x	
Propachlor OXA	H,DP	ACET DP		x	
Propanil	H	ACET	x		
Propazine	H	TRI	x	x	
Resmethrin	I	PY	x		
Simazine	H	TRI	x	x	
Sarafloxacin	A	Q		x	
Stirofos	I	OP	x		
Sulfachloropyridazine	A	SA		x	
Sulfadimethoxine	A	SA		x	
Sulfamerazine	A	SA		x	
Sulfamethazine	A	SA		x	
Sulfamethoxazole	A	SA		x	
Sulfathiazole	A	SA		x	
Sulfotepp	I	OP	x		
Sulprofos	I	OP	x		
Sumithrin (phenothrin)	I	PY	x		
Terbutryn	H	TRI	x		
Tetracycline	A	TC		x	
TFMA (3-trifluromethylaniline)	H,DP	PU DP	x	x	
TFMPU (3-(trifluromethyl)phenylurea)	H,DP	PU DP	x	x	
Thionazin	I	OP	x	x	
Tokuthion	I	OP	x		
trans-Chlordane	I	OC	x		
Trichlornate	I	OP	x		
Trifluralin	H	DNA		x	

Herbicide ■ Insecticide ■ Antibiotic ■ Taste-and-odor problems

[x, USGS approved method; ACET, acetamide; A, antibiotic; DNA, dinitroaniline; DP, degradation product; ELISA, enzyme-linked immunosorbent assay; ESA, ethane sulfonic acid; GC/MS, gas chromatography/mass spectrometry; H, herbicide; I, insecticide; IGR, insect growth regulator; LC/MS, liquid chromatography/mass spectrometry; OC, organochlorine; OP, organophosphate; OPH, organophosphate herbicide; OXA, oxanilic acid; PDZ, pyridazinone; PU, phenylurea; PY, pyrethroid; Q, quinolines; SA, sulfonamide; SYN, synergist; TC, tetracycline; TO, taste and odor problems; TH, thiocarbamate; TRI, triazine]

Herbicides

Herbicides in surface and ground water are a major concern throughout the United States. Because degradation products are formed in the environment and are transported to surface and ground water, it is important to understand herbicide occurrence and the fate of herbicide degradates. Important findings of the 1990s included the persistence of herbicides and their degradation products in water. It has also been shown that the majority of the measured concentrations for many herbicides are in the form of its degradation product. Recently, an enzyme-linked immunosorbent assay method for glyphosate has been added. Glyphosate is a broad spectrum, organophosphate herbicide that kills many plants, including grasses, broadleaf, and woody plants. Glyphosate's global use is increasing with the advent of Roundup Ready® seed that are unaffected by glyphosate.

Acetamides
Acetochlor
Alachlor
Dimethenamid
Flufenacet
Metolachlor
Propachlor
Propanil

Acetamide Degradation Products
Acetochlor ESA
Acetochlor OXA
Alachlor ESA
Alachlor OXA
Dimethenamid ESA
Dimethenamid OXA
Flufenacet ESA
Flufenacet OXA
Metolachlor ESA
Metolachlor OXA
Propachlor ESA
Propachlor OXA

Dinitroanilines
Pendimethalin
Trifluralin

Organophosphate Herbicides
Glyphosate (Roundup™)
Glufosinate (Liberty™)

Organophosphate Herbicide Degradation Product
AMPA (amino methyl phosphonic acid)

Phenylureas
Diuron
Fluometuron
Linuron

Phenylurea Degradation Products
DCA (3,4-dichloroaniline)
DCPMU (3,4-dichloromethylphenylurea)
DCPU (3,4-dichlorophenylurea)
DMFM Demethylfluometuron
TFMA (3-trifluromethylaniline)
TFMPU (3-(trifluromethyl)phenylurea)

Pyridazinone
Norflurazon

Pyridazine Degradation Product
Demethylnorflurazon

Thiocarbamate
Molinate

Triazines
Ametryn
Atrazine
Cyanazine
Metribuzin
Prometon
Prometryn
Propazine
Simazine
Terbutryn

Triazine Degradation Products
Cyanazine acid
Cyanazine amide
Deethylatrazine
Deethylcyanazine
Deethylcyanazine acid
Deethylcyanazine amide
Deethylhydroxyatrazine
Deisopropylatrazine
Deisopropylhydroxyatrazine
Deisopropylprometryn
Didealkylatrazine
Hydroxyatrazine

Insecticides

About 10,000 of the more than 1 million species of insects are crop eating. Of these, approximately 700 species worldwide cause most of the insect damage to crops in the field and in storage. Organochlorines and organophosphates are persistent in the environment and have been found in surface and ground water in both urban and agricultural areas. DDT, an organochlorine, was the first insecticide used on a large scale in the United States. A third class of insecticides, insect growth regulators, mimics the action of an insect growth regulation hormone to interfere with the normal maturation process. This makes it impossible for insects to mature to the adult stages and, thus, prevents them from reproducing. It is used in aquatic areas to control mosquitoes and several types of ants, flies, lice, moths, beetles, and fleas. Pyrethroids are synthetic compounds that duplicate the active principles of the pyrethrum plant. Their application rates are very low. Piperonyl butoxide is a synergist and prolongs the usefulness of some insecticides by curbing the development of resistance. Insecticides studied, as shown below, include the following classes: insect growth regulator, organochlorine, organophosphate, pyrethroid, and synergist.

Insect Growth Regulator
Methoprene

Insect Growth Regulator Degradation Product
Methoprene acid

Organochlorines
cis Chlordane
trans Chlordane
p,p'-DDT
Dieldrin
Endosulfan I
Endosulfan II
Endrin
Alpha HCH
Beta HCH
Delta HCH
Gamma HCH/lindane
Heptachlor
Methoxychlor

Organochlorine Degradation Products
p,p'-DDD
p,p'-DDE
Endosulfan sulfate
Endrin aldehyde
Endrin ketone
Heptachlor epoxide

Organophosphates
Azinfos ethyl
Carbophenothion
Chlorfenvinfos
Chlorpyrifos
Chlorpyrifos methyl
Coumafos
Diazinon
Dichlorvos
Dicrotofos
Ethion
Ethoprop
Fenchlorofos
Fenitrothion
Fensulfothion
Fenthion
Fonofos
Leptofos
Malathion
Merphos
Methidathion
Methyl parathion
Mevinphos
Monocrotofos
Parathion
Stirofos
Sulfotepp
Sulprofos
Thionazin
Tokuthion
Trichlornate

Organophosphate Degradation Product
Dioxazon

Pyrethroids
Resmethrin
Sumithrin (phenothrin)

Synergist
Piperonyl butoxide (PBO)

Antibiotics

Environmental concerns in water quality have changed in the past 5 years to include monitoring programs to address human and veterinary antibiotics in streams. Quinolines, sulfonamides, and tetracyclines, as shown below, have been detected in water samples collected at various sites throughout the United States. Confined animal feeding operations and hospitals are point sources of antibiotics.

Quinolines
Carbadox
Flumequin
Norfloxacin
Oxolinic acid
Sarafloxacin

Sulfonamides
Sulfachloropyridazine
Sulfadimethoxine
Sulfamerazine
Sulfamethazine
Sulfamethoxazole
Sulfathiazole

Tetracyclines
Chlortetracycline
Doxycycline
Minocycline
Oxytetracycline
Tetracycline

Taste-and-Odor Problems

The most commonly reported taste-and-odor problems are the result of cyanobacteria and actinomycetes producing geosmin, an earthy-smelling compound, and 2-methylisoborneol (MIB), a musty-smelling compound. Taste-and-odor problems are not considered a direct threat to public health, but they are a public-relations issue that many water utilities face because consumers generally rely on the taste and odor of their water as the primary indicator of its safety.

Taste-and-odor problems
Geosmin
2-Methylisoborneol (MIB)

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