2014 Pesticide Lake Monitoring Pilot Project

Jerry Sauter
Jim Gray
Pesticide and Fertilizer Division
North Dakota Department of Agriculture

Commissioner Doug Goehring

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ND Department of Health
ND Department of Parks and Recreation
ND Game and Fish Department
ND Geological Survey
ND State University Extension Service
ND State Water Commission
US Department of Agriculture-NRCS
US Fish and Wildlife Service
US Geological Survey

SUMMARY

The North Dakota Department of Agriculture, working in cooperation with the North Dakota Department of Health's Division of Water Quality and the U.S. Geological Survey, completed a pesticide sampling pilot project on North Dakota lakes in 2014. This project consisted of collecting and analyzing samples from 27 lakes throughout the state, one time during mid to late summer. These samples were analyzed by Montana State University Agriculture Experiment Station's Analytical Laboratory for 96 pesticides and pesticide degradates. Atrazine; 2,4-D; and tebuconazole were the most commonly detected pesticides, with notable detections of atrazine and chlorpyrifos.

INTRODUCTION

The North Dakota Department of Agriculture (hereafter "Department") is the lead pesticide regulatory agency in the state through the authority provided in Chapters 4-35, 4-35.1, and 19-18 of the North Dakota Century Code. Under a cooperative agreement with the U.S. Environmental Protection Agency (EPA), the Department is charged with regulating pesticides in the public's interest to ensure that they do not pose a risk of unreasonable adverse effects to human health or the environment. The goal of the Department's Pesticide Water Quality Program (hereafter "Program") is to prevent unacceptable contamination of ground and surface water by pesticides. The Department has a Water Quality Advisory Committee (WQAC) in place to advise them on ground and surface water issues and to guide monitoring programs. Agencies represented on the committee include the ND Department of Health (NDDH), US Department of Agriculture Natural Resource Conservation Service, ND State University Extension Service, US Geological Survey (USGS), ND Geological Survey, ND State Water Commission, US Fish and Wildlife Service, ND Game and Fish Department, and the ND Parks and Recreation Department.

Identifying pesticide surface water issues is a priority for the Department and the WQAC. Before the first monitoring project in 2006, no agency routinely monitored North Dakota's surface waters for pesticides. Including the pilot project in 2006, surface water sampling has focused on rivers and streams and has become more comprehensive. During the 2014 growing season, the NDDH and USGS agreed to collect pesticide samples for the Department as part of their lake sampling program.

The goal of the project was to assess pesticide levels in ND lakes and determine if program expansion is necessary and feasible in the future to include ambient lake sampling for pesticides.

MATERIALS AND METHODS

Pesticide samples and associated field measurements were collected one time in 2014 at 28 sites from mid-July to mid-August. Locations of the sampling sites, site IDs, and sample dates can be found in Table 1 and Figure 1. Lake samples were collected from a boat over the deepest part of each lake. A pesticide sample bottle was placed into a weighted bottle sampler (WBS) and submerged on the upwind side of the boat to a depth of approximately three feet. The bottle was allowed to fill, and then was retrieved, capped, and removed from the WBS. The samples were labeled, carefully packed with bubble wrap and/or rubber mesh and put into a cooler with ice and more packing materials shortly after collection. Coolers containing samples and ice were shipped to the laboratory within seven days of collection using a next-day shipping service.

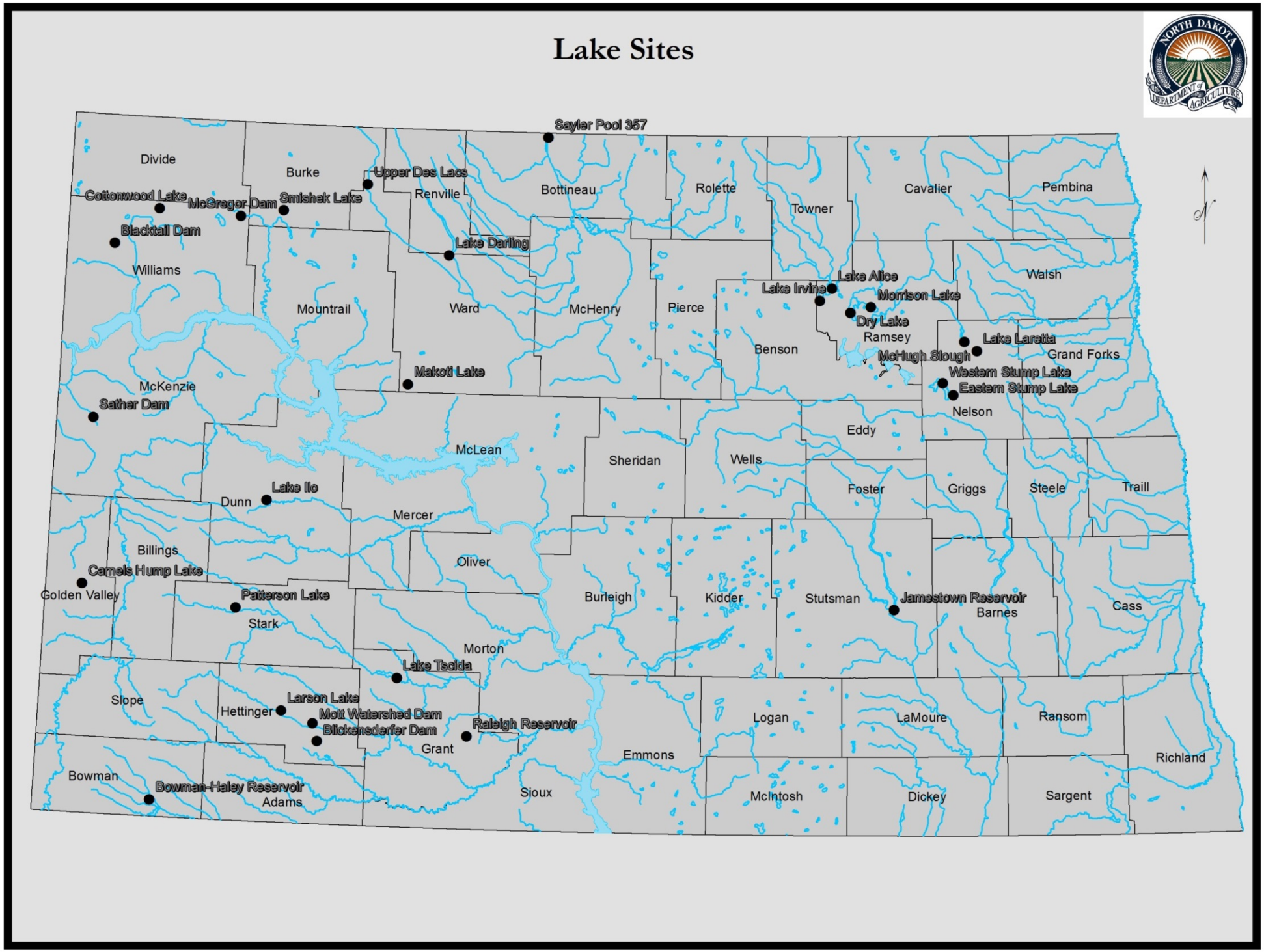
Each pesticide sample consisted of one, 1-L amber glass jar with caps featuring a 1/8" PTFE-faced silicone seal. Sample bottles arrived precleaned according to EPA procedure 1 methods for extractable organic, semivolatile, and pesticide analysis.

Each sample was analyzed for 96 different pesticides and pesticide degradates (Appendix A) by Montana State University's Agriculture Experiment Station Analytical Laboratory. Montana's laboratory developed a customized method titled the MTUniversal method. This method was initially developed to analyze samples for their groundwater monitoring program, but it also fit this project. The method was modeled after the successful USDA PDP Water Survey Program which uses the analytical approach to universalize one method to capture as many compounds as possible at the lowest possible levels with a broader range of acceptable performance. The method was validated according to the requirements of the MT 2008 EPA Quality Assurance Project Plan (QAPP).

Table 1. Lake site IDs, names, and sample dates for the 2014 North Dakota monitoring project.

Site ID	Site Name	Date Sampled
381060	Lake Ilo	7/21/14
380670	Camels Hump Dam	7/21/14
381409	Bowman Haley	7/21/15
380800	Larson Lake	7/22/14
380835	Mott Watershed Dam	7/22/14
380660	Blickensderfer Dam	7/22/14
385350	Raleigh Reservoir	7/22/14
385348	Makoti Lake	7/23/14
380885	Sather Dam	7/23/14
380540	Blacktail Dam	7/23/14
380695	Cottonwood Lake	7/23/14
380820	McGregor Dam	7/23/14
380920	Smishek Lake	7/23/14
384151	Upper Des Lacs Lake	7/30/14
05115500	Lake Darling nr Foxholm, ND	7/29/14
05123990	Sayler Pool 357 nr Westhope, ND	7/29/14
06343500	E.A. Patterson Lake nr Dickinson, ND	7/30/14
06346000	Lake Tschida nr Glen Ullin, ND	7/30/14
06469000	Jamestown Reservoir nr Jamestown, ND	7/28/14
~~05056220~~	~~Sweetwater Lake at Webster, ND (broken)~~	~~8/20/14~~
05056222	Morrison Lake near Webster, ND	8/20/14
05056241	Dry Lake near Penn, ND	8/19/14
05056250	Lake Alice near Churches Ferry, ND	8/19/14
05056260	Lake Irvine near Churches Ferry, ND	8/19/14
05056665	Eastern Stump Lake near Lakota, ND	8/19/14
05056670	Western Stump Lake near Lakota, ND	8/19/14
480339098101300	Lake Laretta near Michigan, ND	8/21/14
480552098145300	McHugh Slough near Lakota, ND	8/21/14

Figure 1. 2014 Lake sampling sites.



RESULTS AND DISCUSSION

There were a total of 27 lake samples analyzed for 96 different pesticides and pesticide degradates in 2014. Of the 96 pesticides analyzed, 49 different pesticides were present in at least one of the samples. Several pesticides were present in a high percentage of the samples as indicated in Table 2. Atrazine; 2,4-D; tebuconazole; MCPA; flucarbazone sulfonamide (FSA); and pyrasulfotole were present in over 70% of the samples collected.

Table 2. Common pesticides detected in the 2014 North Dakota lake monitoring project.

Common pesticides detected in lakes in 2014						
	Quantifiable Detects		Qs (Present but below reporting limit)		Total samples with quantifiable detects and Qs	
Analyte	Number	Percent of all samples	Number of Qs	Percent of all samples	Number	Percent of all samples
Atrazine	27	100	0	0	27	100
Deethyl atrazine (atrazine breakdown product)	27	100	0	0	27	100
2,4-D	20	74	6	22	26	96
Hydroxy atrazine (atrazine breakdown product)	18	66	7	25	25	92
Tebuconazole	13	48	11	40	24	88
MCPA	15	55	8	29	23	85
Pyrasulfotole	13	48	8	29	21	77
FSA (flucarbazone breakdown product)	15	55	5	18	20	74
Propiconazole	9	33	8	29	17	62
Bentazon	15	55	1	3	16	59
Flucarbazone	12	44	3	11	15	55
Deisopropyl atrazine (atrazine breakdown product)	5	18	10	37	15	55
Prometon	7	25	8	29	15	55
IMAM	9	33	4	14	13	48
Acetochlor OA (acetochlor breakdown product)	5	18	6	22	11	40
Fluroxypyr	5	18	6	22	11	40
Dimethenamid	3	11	4	14	7	25
Metolachlor ESA (metolachlor breakdown product)	3	11	4	14	7	25
Metalaxyl	0	0	7	25	7	25
Chlorpyrifos*	2	100	0	0	2	100

*Because of sample matrix interference, chlorpyrifos was only successfully analyzed in two samples.

Data were compared to EPA established aquatic life benchmark (ALB) values and human health maximum contaminant level (MCL) values. A high percentage of the detections were at levels well below the MCLs and/or ALBs, indicating that they were at levels that do not pose a significant risk to human health or aquatic ecosystems. Detections at 20% or more of the lowest of either the MCL or ALB values were further reviewed.

There were no detections at or above 20% of an established MCL. However, there were three detections of two pesticides at 20% or more of the lowest ALB value. The insecticide chlorpyrifos was detected twice and the herbicide atrazine was detected once as detailed in Table 3.

Table 3. 2014 Lake sampling detections at 20% or more of the lowest ALB

Site Name	Site ID	Sample Date	Analyte	Level	ALB (ppb)
Makoti Lake nr Makoti, ND	385348	7/23/2014	Chlorpyrifos	0.045	0.04
Sayler Pool 357 nr Westhope, ND	05123990	7/29/2014	Chlorpyrifos	0.039	0.04
Jamestown Reservoir nr Jamestown, ND	06469000	7/28/2014	Atrazine	0.75	1.00

Looking at values at or above 20% of an ALB is a very conservative means to filter data and does not automatically indicate significant risk to aquatic ecosystems. In looking for levels that may pose risk, results were further reviewed to identify instances in which an ALB or MCL had been exceeded. No pesticides were detected at concentrations exceeding an MCL, although there was one detection above an ALB.

Chlorpyrifos was detected at 0.045 ppb at Makoti Lake near Makoti, ND on July 23, 2014. The lowest toxicity endpoint for chlorpyrifos is 0.04 ppb which is the no observed adverse effect concentration (NOAEC) for assessing chronic risk to freshwater invertebrate populations (Chlorpyrifos RRED 2000). Further review indicates the lowest observed adverse effect concentration (LOAEC) is 0.08 ppb, which, after chronic exposure, greatly reduced survival and offspring production in *Daphnia magna* in the referenced study. The highest concentration detected in lakes in 2014 was 0.045 ppb which is 1.125 times higher than the NOAEC and 1.778 times lower than the LOAEC. Samples were not collected before and after chlorpyrifos detections, so it is impossible to determine how long the chlorpyrifos level persisted. Comparing collected data to chronic NOAEC toxicity values is a very conservative means to estimate risk to ND lakes. A sample result exceeding a chronic NOAEC does not indicate significant risk from chlorpyrifos use, but it does indicate that additional monitoring may be beneficial to try and determine spike levels and persistence. There is no EPA established drinking water standard for chlorpyrifos.

CONCLUSION

The goal of this project was to sample a subset of ND lakes and define what (if any) pesticides are present to determine if additional lake sampling should be completed in the future. Although no pesticides were found at levels that pose a significant risk to human health or aquatic life, results indicate that some pesticides were present and reaching levels that need to be monitored. As budgets allow, additional lake sampling may be incorporated into the pesticide surface water monitoring program.

REFERENCES

U.S. EPA Fate and Environmental Risk Assessment Chapter. 2000. Reregistration Eligibility Science Chapter For Chlorpyrifos. U.S. EPA. Washington D.C.

Appendix A. List of analytes, common trade names, and laboratory reporting limit.

List of analytes 2014			
Analyte	**Common Trade Names***	**Type**	**Reporting Limit (ppb)**
2,4-D	2,4-D, Curtail	H	0.00450
Acetochlor	Surpass, Harness	H	0.14000
Acetochlor ESA	degradate	D	0.01000
Acetochlor OA	degradate	D	0.00420
Alachlor	Intrro, Lariat, Lasso	H	0.11000
Alachlor ESA	degradate	D	0.01100
Alachlor OA	degradate	D	0.00340
AMBA (mesotrione metabolite)	degradate	D	0.02100
Aminocyclopyrachlor	Method, Perspective	H	0.02500
Aminopyralid	Cleanwave	H	0.01500
Atrazine	Aatrex	H	0.00220
Azoxystrobin	Quadris	F	0.00260
Bentazon	Basagran	H	0.00110
Bromacil	Hyvar, Bromax	H	0.00410
Bromoxynil	Huskie, Buctril	H	0.00600
Carbaryl	Sevin, Savit	I	0.00400
Chlorpyrifos	Lorsban, Dursban	I	0.03100
Chlorsulfuron	Finesse, Glean	H	0.00560
Clodinafop acid	Discover NG	H	0.01300
Clopyralid	Stinger, Curtail	H	0.02200
Clothiandin	Poncho	I	0.01600
Deethyl atrazine	degradate	D	0.00170
Deethyl Deisopropyl Atrazine (DEDIA)	degradate	D	0.10000
Deisopropyl atrazine	degradate	D	0.01000
Dicamba	Banvel	H	0.22000
Difenoconazole	CruiserMaxx, InspireF		0.01100
Dimethenamid	Outlook	H	0.00300
Dimethenamid OA	degradate	D	0.00380
Dimethoate	Cygon, Roxion	I	0.00110
Disulfoton sulfone	degradate	D	0.00660

List of analytes 2014

Analyte	Common Trade Names*	Type	Reporting Limit (ppb)
Diuron	Direx, Karmex	H	0.00530
Fluoroethyldiaminotriazine (FDAT)	degradate	D	0.00530
Fipronil	Regent	I	0.00120
Flucarbazone	Everst, Prepare	H	0.00120
Flucarbazone sulfonamide (FSA)	degradate	D	0.00097
Flumetsulam	Python	H	0.02900
Fluroxypyr	Starane	H	0.01600
Glutaric Acid	degradate	D	0.00740
Hydroxy atrazine	degradate	D	0.00400
Halosulfuron methyl	Permit	H	0.00600
Hexazinone	Velpar	H	0.00150
Imazamethabenz methyl acid metabolite (IMAM)	degradate	D	0.00250
Imazamethabenz methyl ester (IME)	degradate	D	0.00100
Imazamox	Raptor, Beyond	H	0.00570
Imazapic	Plateau	H	0.00300
Imazapyr	Imazapyr, Lineage	H	0.00350
Imazethapyr	Authority Assist, Pursuit	H	0.00400
Imidacloprid	Touchstone PF	I	0.00180
Indaziflam	Alion, Specticle	H	0.00200
Isoxaben	Gallery, Snapshot	H	0.00210
Isoxaflutole	Corvus, Balance Flexx	H	0.13000
Malathion	Malathion, Cythion	I	0.02800
Malathion oxon	degradate	D	0.00120
MCPA	MCP	H	0.00230
MCPP	Encore, Trimec	H	0.00220
Metalaxyl	Hi-Yield, Ridomil	F	0.00350
Methomyl	Lannate	I	0.00160
Methoxyfenozide	Intrepid	I	0.00230
Metolachlor	Dual Magnum	H	0.01200
Metolachlor ESA	degradate	D	0.00250
Metolachlor OA	degradate	D	0.02100
Metsulfuron methyl	Ally, Cimarron	H	0.01000
Nicosulfuron	Accent, Steadfast	H	0.01100
NOA 407854 (Pinoxaden metabolite)	degradate	D	0.00520
NOA 447204 (Pinoxaden metablolite)	degradate	D	0.01000
Norflurazon	Solicam	H	0.02000

List of analytes 2014			
Analyte	**Common Trade Names***	**Type**	**Reporting Limit (ppb)**
Norflurazon desmethyl	degradate	D	0.02000
Oxamyl	Vydate	I	0.01000
Parathion methyl oxon	degradate	D	0.01200
Phorate sulfone	degradate	D	0.00610
Phorate sulfoxide	degradate	D	0.00150
Picloram	Tordon	H	0.14000
Picoxystrobin	Approach	F	0.00510
Prometon	Pramitol	H	0.00100
Propiconazole	Banner, Tilt, Radar	F	0.01000
Prosulfuron	Peak, Spirit	H	0.00500
Pyrasulfatole	Huskie, Wolverine	H	0.00930
Pyroxsulam	GR1, Powerflex	H	0.01300
Saflufenacil	Sharpen	H	0.01000
Simazine	Princep	H	0.00260
Sulfentrazone	Spartan	H	0.03500
Sulfometuron methyl	Lineage, Oust	H	0.00250
Sulfosulfuron	Maverick, Outrider	H	0.00540
Tebuconazole	Folicur	F	0.00700
Tebuthiuron	Spike	H	0.00110
Tembotrione	Capreno, Laudis	H	0.01800
Terbacil	Sinbar	H	0.00240
Terbufos sulfone	degradate	D	0.00530
Tetraconazole	Domarck, Eminent	F	0.00390
Thiamethoxam	CruiserMaxx, Meridian	I	0.02000
Thifensulfuron	Supremacy Harmony	H	0.01100
Tralkoxydim	Achieve	H	0.00510
Tralkoxydim acid	degradate	D	0.00500
Triallate	Far-Go	H	0.30000
Triasulfuron	Dally, Rave	H	0.00550
Tricolpyr	Garlon	H	0.01100

*Common trade names do not represent all trade names containing an active ingredient. Trade names chosen are for example purposes only and this list is not endorsing or making any recommendations.

H=Herbicide; I=Insecticide; F=Fungicide; D=Degradate (breakdown product)